INTERNATIONAL CONFERENCE

WATER IN THE GAS PHASE

WGP 98

June 21 - 24, 1998

University of Marne la Vallée

PARIS FRANCE

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WATER IN THE GAS PHASE

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International Conference

WATER IN THE GAS PHASE

PROGRAM

Sunday, June 21

10.00 - 15.30

Registration at the Copernic building of the UMLV, posters installation

Sessions will be held at the Copernic building in the auditorium on the ground floor, posters will be displayed close to the auditorium during the whole meeting

15.30 - 15.45 Opening

15.45 - 16.15 Jacques Crovisier
H_2O in comets

16.15 - 16.45 Peter Bernath
Laboratory spectroscopy of water

16.45 - 17.15 Laurent Coudert
Spectroscopy of water vapor : the rotational energy pattern of a floppy triatomic molecule

17.15 - 17.45 Samuel Leutwyler
Structures, isomers and torsional interconversions of small water clusters

17.45 - 18.15 Elise Kochanski
Study of electronic states of $H_5O_2^+$

19.00 Buffet in the Copernic building

Monday, 22 June

8.30 - 9.30	Poster session
9.30 - 10.00	Michele Parrinello Ab initio simulation of proton transfer and water clusters
10.00 - 10.30	Richard Saykally Studies of water clusters by terahertz and IR cavity ringdown spectroscopy : force fields
10.30 - 11.00	Coffee
11.00 - 11.30	Friedrich Huisken Vibrational spectroscopy of free and adsorbed water clusters
11.30 - 11.50	Leo Lehr Dynamics in $I^-(H_2O)_n$ clusters
11.50 - 12.10	Bertrand Guillot Structure of supercritical water
12.10 - 12.30	Yulia Novakovskaya Water cluster anions as the model of hydrated electron
12.30	Lunch in Copernic building
14.00 - 14.30	Claude Camy-Peyret and Jean-Marie Flaud Low pressure flame H_2O spectra
14.30 - 15.00	Kit Bowen Water dipole cluster anions studied by photoelectron spectroscopy
15.00 - 15.30	Ad van der Avoird Tunneling dynamics and spectra of water clusters
15.30 - 16.00	Udo Buck Excitation spectra of intra and intermolecular motions of water clusters
16.00 - 16.30	Coffee

16.30 - 17.00 Claude Leforestier
VTR energy transfer of water dimer : influence of the internal vibrations

17.00 - 17.30 Zlatko Bacic
Quantum dynamics of coupled torsional vibrations in $(H_2O)_3$, $(H_2O)_4$ and their isotopomers : energy levels, tunneling splittings and vibrationally averaged rotaional constants

17.30 - 17.50 Bernd Brutschy
Water clusters attached to benzene derivatives : structure, binding energy, ion-chemistry

17.50 - 18.10 Karl Kleinermanns
Electronic spectroscopy of phenol(water)$_{1-2}$ clusters : structures and intermolecular vibrations

Tuesday, 23 June

8.30 - 9.30 Poster session

9.30 - 10.00 Jonathan Tennyson
First principle calculation of spectrum of hot water

10.00 - 10.30 Oleg Polyansky
Analysis of hot water spectra in sunspots and the laboratory

10.30 - 11.00 Coffee

11.00 - 11.30 Laurence Rothman
Evaluation of water vapor line-parmeter databases : HITRAN and HITEMP

11.30 - 12.00 Reinhard Schinke
Photodissociation of water

12.00 - 12.30 Wilfried Meyer
Dynamical polarizabilities of water and long range interactions

12.30 Lunch in Copernic building

14.00 - 14.30 David Nesbitt
Breaking bonds in water and water clusters : zero-point and vibrationally mediated photofragmentation dynamics

14.30 - 15.00 Welford Castleman
Solvation effects on reactions in clusters

15.00 - 15.30 David Schwenke
Ab-initio calculations of water line strengths

15.30 - 15.50 Gereon Niedner-Schatteburg
Reactivity of charged water clusters

15.50 - 16.20 Coffee

16.20 - 16.50 Vladimir Tyuterev
Generating function model for calculation of high resolution spectra of water

16.50 - 17.20 Jim Coe
OH^- and H_3O^+ recombination as a function of water solvent

17.20 - 17.40 Mark Johnson
Electron and ion hydration in clusters

17.40 - 18.00 Timothy Zwier
The spectroscopy and dynamics of water solvation in small biomolecules-$(water)_n$ clusters

19.30 Departure by bus for the Conference riverboat dinner, on the Seine

Wednesday, 24 June

8.30 - 9.30 Poster session

9.30 - 10.00 Barry Lutz
H_2O^+ in comets

10.00 - 10.30 Suehiro Iwata
Structure and spectroscopy of water cluster anions

10.30 - 11.00 Coffee

11.00 - 11.30 L.N. Sinitsa
Study of highly excited states of water isotopomers in Tomsk

11.30 - 11.50 Sotiris Xantheas
Interplay between cooperativity and hydrogen bonding network in water clusters

11.50 - 12.10 Hans-Juergen Neusser
Structure, intermolecular dynamics and binding energy of organic molecule water complexes

12.10 - 12.40 Michel Desbois
Water vapor in the atmosphere : radiative effects and role on the climate system

12.45 Lunch in Copernic building

14.00 - 14.20 Martin Schuetz
Local treatment of electron correlation in water clusters

14.20 - 14.40 D.E. Benoit and D.C. Clary
Quantum simulation of negatively charged water clusters and solvated organic molecules

14.40 - 15.00 Roger Miller
The infrared spectroscopy and dynamics of water clusters

15.00 - 15.20 James Haynes
Acid ionized HBr in a four-water cluster

15.20 - 15.50 Michel Vervloet and Pavel Rosmus
Spectroscopy of H_2O^+

15.50 - 16.00 Concluding remarks and end of the Conference

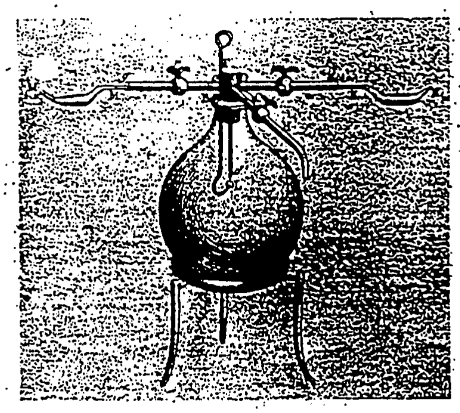
Reminiscence

Aristotle included water among the four elements, alongside earth, air, and fire. Not until the 18th century was it established that earth and air were mixtures, and that fire was simply the manifestation of chemical change.

In 1781 Priestley synthesized the last one of the Aristotle's elements, and shortly afterward Lavoisier and Cavendish succeeded in decomposing liquid water into "ordinary air" (oxygen) and "inflammable air"(hydrogen).

The 18th century debates, such as the one between Cavendish and Lavoisier, were quite harsh despite the acknowledged personal modesty of the protagonists.

A.L. Lavoisier, Mém.Acad.France 1781,486
(..comme on a voulu élever quelques doutes sur l'antériorité de cette découverte...)



..Mais comme il n'est pas moins vrai en physique qu'en géométrie que le tout est égal à ses parties, de ce que nous n'avions obtenu que de l'eau pure dans cette expérience,nous nous sommes crus en droit d'en conclure que le poids de cette eau était égal à celui des airs qui avaient servi à le former.

78 years of the "hydrogen bonds"

"the hydrogen nucleus held between two octets constitues a weak bond"

W.M. Latimer and W.H. Rodebush,
Polarity and ionization from the standpoint of the Lewis theory of valence
J.Am.Chem.Soc. 42,1419 (1920)

50 years later Ratner and Sabin wrote:
(The Wave Mechanical Treatment of Hydrogen Bonded Systems, in Wave Mechanics, Butterworths, London 1973)

Hydrogen bonds are liaisons dangereuses for theoreticians. Their characterization and description continues to challenge physical science. The importance and uniqueness of hydrogen bonds in the nature stems from their omnipresence and their weakness.

A WONDER WATER FROM KAZAKHSTAN

	Anomalous water	Normal water
Melting point	- 40°C	0°C
Boiling point	250°C	100°C
Density	1.4	1.0
Magnetic susceptibility	positive	negative
Viscosity	15cP	1cP

Etc.

Millions of dollars (and rubles?) were spent in the pursuit of anomalous water. A warning that this polywater might be the most dangerous material on earth altered the news media, and from then on much of the scientific debate was carried on the pages of newspapers.

CONTENTS : TALKS

POSTERS

TALKS

SUNDAY

« Water in comets »

Jacques Crovisier

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Water is the major constituent of cometary ices. Its sublimation governs the activity of comets when they approach the Sun and develop a tail and an atmosphere. Water plays an important role in photolytic heating and radiative cooling of cometary atmospheres.

Cometary water is very deffilult to observe from the ground, where photolytic secondary products (OH, H, O) or photoionization products (H_2O^+, H_3O^+, OH^+) are rather observed. Cometary water could be observed directly from high-altitude aircraft, space probes, and recently from the Infrared Space Observatory (ISO). Several infrared hot bands of water could also be observed from the ground, taking benefit of recent high-resolution sensitive inst,rumentation.

The ro-vibrational lines of cometary water are emitted through fluorescence excited by the solar radiation field. Modelling of the whole fluorescence cascades requires the knowledge of band strengths, including those of hot bands. High-resolution spectra of the ν3 water band region of water permit to study physical conditions in cometary matter: the rotational temperature of water and its spin temperature from the ortho-to-para ratio.

Future space facilities will allow us to study cometary water. Submillimetre satellites (SWAS, ODIN, FIRST) will observe rotational lines of water. The ROSETTA space probe, which will orbit comet Wirtanen from a distance of a few kilometres, will be equipped with a small radio telescope (MIRO) which will observe the fundamental rotational lines of water and its isotopes, and by an infrared spectrometer (VIRTIS-H) dedicated to the 2-5 μm spectral region, including the ν3 water band region.

TALK 2
Sunday 16.15 - 16.45

« Laboratory Spectroscopy of Water »

P. Bernath

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Waterloo, Ontario
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The general status of the laboratory spectroscopy of water vapor will be reviewed from the microwave to the near UV regions. In our laboratory, many infrared emission spectra of hot water (and deuterated isotopomers) have been recorded with a Fourier transform spectrometer. These laboratory data have proved to be very useful in identifying water vapor in various astronomical sources such as sunspots (1). The assignment of such complex spectra presented a strong challenge to theory and ultimately led to a doubling of the known energy levels of water (2).

More recently new absorption spectra of water (and deuterated isotopomers) have been recorded using a 50 meter base path multiple reflection cell. These new Fourier transform spectra cover the near infrared, visible and near UV region and represent a major improvement on the existing work.

1. L. Wallace, P. Bernath, W. Livingston, K. Hinkle, J. Busler, B. Guo and K.-Q. Zhang, Water on the Sun, Science 268, 1155-1158 (1995).
2. O.L. Polyansky, N.F. Zobov, S. Viti, J. Tennyson, P.F. Bernath and L. Wallace, Water on the Sun: line assignments based on variational calculations, Science 277, 346-348 (1997).

« SPECTROSCOPY OF WATER VAPOR: THE ROTATIONAL ENERGY PATTERN OF A FLOPPY TRIATOMIC MOLECULE »

L. H. Coudert

Laboratoire de Photophysique Moléculaire, C.N.R.S., Bât.210,
Université Paris-Sud, 91405 Orsay Cedex, France

The calculation of the energy levels of non-rigid molecular systems, i.e., systems displaying large amplitude motions, has always been tedious and complicated. This is especially true for the water molecule which remains a challenge for molecular theorists.

In the present paper we will first discuss various problems related to the spectroscopy of the water molecule. We will try to understand why the the rotational energy levels of the water molecule are different from those of a normal molecule, i.e., a rigid molecule. The interaction of the large amplitude bending v2 mode with the overall rotation of the molecule will be examined and shown to be the cause of the unusual rotational energy level pattern as well as the origin of the so-called anomalous centrifugal distortion. As a result, the approaches which are usually used for rigid molecules can not be applied to the case of the water molecule and special theoretical treatments must be designed.

An overview of the various approaches which have been set-up so far to account for this anomalous distortion will afterwards be given. Their accuracy as well as their validity will be discussed in terms of the number of degrees of freedom considered in the Hamiltonian. Special emphasis will be given to a newly developed 4-dimensional approach, the Bending-Rotation Hamiltonian approach, which, because it only involves matrix elements with tractable analytical expressions, lead to fast computer codes and allows us to reproduce experimental data within their experimental uncertainty. Recent results obtained with this approach when fitting high lying rotational energy levels will be presented.

1. C. Camy-Peyret and J.-M. Flaud, *J. Molec. Spectrosc.*, **59,** 327 (1976).
2. L. H.Coudert, *J. Molec. Spectrosc.*, **181,** 246 (1997).
3. O. L. Polyansky, J. Tennyson and P. F. Bernath, *J. Molec. Spectrosc.*, **186,** 213 (1997).
4. O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, *J. Molec. Spectrosc.*, **186,** 422 (1997).
5. R. Lanquetin, *Thèse de l'Université Paris Nord,* 1997.

TALK 4
Sunday 17.15 - 17.45

« Structures, isomers and torsional interconversion of small water clusters »

Samuel Leutwyler, Wolfgang Mohr, Martin Lozada and Stephan Graf

Departement fueÄr Chemie und Biochemie, Universiaet Bern
Freiestr. 3, 3000 Bern 9, Switzerland

The global minimum structures of the water trimer, tetramer and pentamer are cyclic and homodromic. For the hexamer, the situation is still not clear, but the cyclic homodromic structure is certainly one of the energetically low-lying minima. For the trimer and tetramer, the oxygen atoms lie in a plane, whereas the equilibrium structure of the water pentamer is puckered, similar to cyclopentane, and that of the hexamer is similar to the "chair" conformer of cyclohexane. The non-hydrogen bonded H atoms point alternately "up" or "down" with respect to the oxygen framework.

The lowest energy structural interconversion paths of these cyclic water clusters are all associated with torsional or flipping motions of the free H atoms. These motions interconvert structurally equivalent global minima on the intermolecular potential energy surface of the cyclic cluster. There are six such minima for water trimer, two for the water tetramer, ten for the pentamer and two for the hexamer, if breaking of hydrogen bonds is assumed to be not feasible. These interconversion pathways will be discussed.

For the trimer and pentamer, the barriers along the flipping interconversion pathway are very low, strongly affecting the intermolecular torsional vibrations: the torsional frequencies are lowered by a factor of ten or more relative to the harmonic values, influencing the far-infrared spectra, the torsional density of states and the vibrational entropy of these clusters. For the water tetramer and hexamer, there are framework deformation (translational-type) modes which are at lower frequencies than the torsional modes, but these do not lead to structural interconversion and can be treated to a good approximation as harmonic.

References:

T. Buergi, S. Graf, S. Leutwyler and W. Klopper, J. Chem. Phys. 103, 1077 (1995).

W. Klopper, M. Schuetz, H. P. Luethi and S. Leutwyler, J. Chem. Phys. 103, 1085 (1995).

M. Schuetz, W. Klopper, H. P. Luethi and S. Leutwyler, J. Chem. Phys. 103, 6114 (1995).

D. Sabo, Z. Bacic, T. Buergi and S. Leutwyler, Chem. Phys. Lett. 244, 283 (1995).

D. Sabo, Z. Bacic, S. Graf and S. Leutwyler, Chem. Phys. Lett. 261, 318 (1996).

« LOWEST electronic states of small protonated hydrates »

S. Klein, E. Kochanski, A. Strich, A. Sadlej[a]

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Email : kochansk@quantix.u-strasbg.fr
[a] Lund, Sweden, now in Torun, Poland

Though a huge amount of work is available on protonated hydrates, it generally concerns the ground state and information on the excited states is scarce. A very few theoretical papers deal with electronic excited states of the smallest cluster, the oxonium ion H_3O^+, but nearly nothing on the protonated dihydrate $H_5O_2^+$. This is probably due to the difficulties encountered in both experiments and theory. However, the interest for such excited systems is rising, in particular in ultra-fast (femtosecond) spectroscopy and to explain chemical processes involving proton transfer in excited states. We can anticipate that theoretical studies will also appear in the near future.

We recently started a theoretical study on the lowest electronic states of $H_5O_2^+$. CASSCF/CASPT2 ab initio calculations have been done using large diffuse and polarized basis sets able to correctly describe such electronic excited states. The $^1A''$ and $^3A''$ states have been considered (1).

The study of $H_5O_2^+$ requires the knowledge of its two subsystems H_2O and H_3O^+. In particular their electric properties play an important role in the stabilization of the complex through intermolecular interactions. They have been computed using the finite-field perturbation theory. A special attention has been paid to the correlation energy effect, which is very important for all three systems.

About forty theoretical papers have been published on the excited electronic states of H_2O since 1969. For most of them the main motivation was to understand the origin of the abnormal high degree of rotational excitation in OH. As a consequence, they often considered the excited state B $^1A_1$, which is not the lowest excited state but can have a linear structure. Surfaces are presented, together with vertical or adiabatic excitations for many other states. Information on the dipole moment and polarizability components are available only in 5 papers, in particular for the lowest $^1A_1$, $^1B_1$ and $^3B_1$ states. Their main features were qualitatively described in an early pioneer work (2) but accurate calculations became feasible only recently (3-6). These electric properties are very different in the ground and excited states. The dipole moments have opposite sign; the polarizability tensor, nearly isotropic in the ground state, is highly anisotropic in the excited states, with huge values for the $^1B_1$ and $^3B_1$ Rydberg states. From a theoretical point of view, it is absolutely necessary to use diffuse and polarization functions, and the contribution of the dynamic correlation is important. The geometry is not very different in the three lowest states (C_{2v}).

The first excited states of the oxonium ion are valence states. The first excited states are planar, the ground state slightly pyramidal. This involves a change in the dipole moment. The polarizability components are slightly smaller and slightly more anisotropic than those of water for the ground state. They are very large and highly anisotropic in the first singlet and triplet excited states, though they are somewhat smaller than for the excited states of water (7).

Except a short semi-empirical note based on crude approximations (8), no theoretical information was available on the excited states of $H_5O_2^+$ before our own studies. This note suggested that the photodissociation process could participate to the rapid decrease in concentration of $H_3O^+(H_2O)_n$ions in the atmosphere observed above 82 km. The two lowest $^1A''$ and $^3A''$ excited states of $H_5O_2^+$ are Rydberg states (1). As for the ground state, two geometries (C_2 and C_s, similar for both excited states) are nearly

degenerate, allowing an easy transfer of the proton (or of the central Hydrogen atom). The distance between the two Oxygen atoms is much larger in the excited states (around 4 Å) than in the ground state (around 2.4 Å). In the Cs structure, we can identify an oxonium unit in the ground state and a water unit in its first excited state. The electric properties of the excited states are, again, very different of those of the ground state. The polarizability tensor, weakly anisotropic in the ground state, becomes highly anisotropic in the excited states, with a huge component along the intermolecular axis (more than 400 or 500 a.u.). The electrostatic energy contribution is important in the ground state, while the excited states are mainly stabilized by the dispersion energy. The excitation energy shows that the photoexcitation of $H_5O_2^+$ is probably possible in the atmosphere.

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(1) S. Klein, E. Kochanski, A. Strich, A.J. Sadlej, J. Phys. Chem. A 101 (1997) 4799.
(2) M. van Hemert, A. van der Avoird, J. Chem. Phys., 71 (1979) 5310
(3) M. Urban, A.J. Sadlej, Theor. Chim. Acta, 78 (1990) 189
(4) A. Balková, R.J. Bartlett, J. Chem. Phys., 99 (1993) 7907
(5) O.N. Ventura, Z. latajka, H. Ratajczak, W.J. Orville-Thomas, J. Molec. Struct.(Theochem), 334 (1995) 127
(6) S. Klein, E. Kochanski, A. Strich, A.J. Sadlej, Theor. Chim. Acta 94 (1996) 75;
(7) S. Klein, E. Kochanski, A. Strich, Chem. Phys. Lett. 260 (1996) 34;
(8) T.F. Thomas, T.L. Rose, J.F. Paulson, J. Chem. Phys., 71 (1979) 552

MONDAY

« Proton transfer in water : cluster and bulk »

Michele Parrinello

TALK 7
Monday 10.00 - 10.30

« WATER CLUSTERS »

Richard J. Saykally

Department of Chemistry, University of California, Berkeley, CA 94720-1460, U.S.A.

Clusters of H_2O and D_2O as large as hexamer (and possibly octamer) have been studied in much detail by terahertz laser VRT spectroscopy[a] Torsional and bifurcation dynamics of the quasiplanar ring clusters have been quite thoroughly characterized. Current experimental efforts are centered in the "translational band" region of the liquid (ca. 150 cm-1).

IR Cavity Ringdown Laser Absorption Spectroscopy[b] has been employed for the study of monomer distortion and cooperativity effects in these clusters. The D_2O stretch and H_2O bending vibrations have been characterized for the first time in the gas phase.

A global 6-D water pair potential has been obtained by fitting VRT and microwave data for the dimer, using Leforestier's Wigner pseudospectial formalism.[c]

[a] K. Liu, J.D. Cruzan, and R.J. Saykally, Science **271**, 929 (1996);
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M.R. Viant, J.D. Cruzan, D.D. Lucas, M.G. Brown, K. Liu, and R.J. Saykally, J. Phys. Chem. A **101**, 9032 (1997).
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J.B. Paul, C.P. Collier, J.J. Scherer, A. O'Keefe, and R.J. Saykally, J. Phys. Chem. A **101**, 5211 (1997);
J.B. Paul, R.A. Provencal, and R.J. Saykally, J. Phys. Chem. A (submitted 1998).
[c] C. Leforestier, L.B. Braly, K. Liu, M.J. Elrod, and R.J. Saykally, J. Chem. Phys. **106**, 8527 (1997).

« Vibrational Spectroscopy of Free and Adsorbed Water Clusters »

F. Huisken

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D-37073 Göttingen, Germany

The vibrational spectroscopy of small water clusters [$(H_2O)_n$, n = 2,3,4,5] has been studied in the O-H stretching region by means of the molecular beam depletion technique which is based on the vibrational predissociation of the weakly bound complexes after infrared laser excitation. A unique feature of the present study is the incorporation of a size selection which is achieved by dispersing the water clusters with a secondary rare gas beam and measuring the laser-induced depletion as a function of the scattering angle. In this way, various absorption bands observed below 3600 cm^{-1} could be assigned for the first time to the bonded O-H stretches of specific water clusters (n = 2,3,4,5). In another experiment, the water clusters were embedded in ultracold liquid helium clusters (T = 0.4 K). Due to the low temperature, much better resolution could be obtained. In general it was found that the helium cluster constitutes an ideal (nano-)matrix inducing only minor shifts in the rotational-vibrational levels, as a result of the *weak* interaction of the water cluster with the environment. A third experiment was devoted to the investigation of medium-sized water clusters [$(H_2O)_n$, $15 < n < 40$]. Comparison with the literature spectra of liquid water surfaces revealed that the water clusters produced in our study were liquid. In order to obtain more information on the internal structure of the water clusters, they were doped with single methanol molecules. By analyzing the mass distribution of the dissociation products after excitation of the C-O stretch of the methanol chromophore, we have found that the water clusters were composed of loosely bound subunits, a result which seems in perfect agreement with their liquid nature. The detailed spectroscopic study of the methanol molecule revealed that it was attached to the water cluster via three hydrogen-bonds with the methyl group pointing away from the cluster surface.

« The transition from dipole bound to solvated electron: Dynamics of charge transfer to solvent precursor states in mass selected iodine water anion clusters »

L. Lehr, R. Weinkauf,

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M. T. Zanni, B. J. Greenblatt, D. M. Neumark,

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By UV photoexcitation of mass selected $I^-(D_2O)_n$ (n=2, 4-8) anion clusters it is possible to populate cluster precursor states of the charge transfer to solvent state (CTTS) well known for iodine water. The dynamics of the cluster CTTS precursor state is monitored by femtosecond pump-probe two-photon photoelectron spectra. They show electron energy shifts, changes of electron energy distribution and non-monotonous variations of electron intensity in dependence on pump-probe delay. This features are interpreted as stabilization of the excess electron by interstate dynamics and/or by solvent reorientation in the excited CTTS precursor state. Whereas in the $(I(D_2O)_n)^-$ n = 2, 4 anion cluster a narrow energy distribution of the emitted electrons indicates the excited CTTS precursor state to be of dipole bound character, with growing cluster size the measured photodetachment photoelectron spectra show complicated time dependence. For n = 5 and 6 after initial excitation of a dipole bound state the surplus electron is stabilized by radiationless relaxation to a state, which considerably differs in structure from the neutral ground state. This indicates the presence of the electron inside the cluster. This interpretation as an interstate transition is supported by the observed non-monotonous time behavior of integral electron intensities, which can be interpreted as changes of the electronic transition moment during cluster reorganization. The interstate dynamics is faster than 600 fs for $(I(D_2O)_5)^-$ and slows down to 1 ps for cluster size n = 6. For n ≥ 7 a state of «wet electron» character is supposed to be directly populated by the pump photoexcitation. The subsequent electron stabilization on the picosecond time scale is a reorientation dynamics of the water shell on a single electronic surface. All CTTS precursor states have a positive electron affinity. The monotonous decrease of electron intensity at longer pump-probe delay times is attributed to a population decay due to vibrational autodetachment (n = 2, 4), electron recombination (n>6) or both (n = 5, 6).

TALK 10
Monday 11.50 - 12.10

« Structure of supercritical water »

Bertrand Guillot

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Due to its importance in many industrial applications, supercritical water was in the last decade the purpose of a great number of experimental and theoretical works attempting to elucidate the structure and the dynamics of the hydrogen bonds in this state. The major part of these new studies have been initiated by the results coming from computer simulations. An important prediction of these simulations was that above the critical point (374°C) in dense fluid water (0.5 - 0.7 g/cm3) hydrogen bonding is still present. In 1993 an article published in nature (Postorino et al., 366, p668) presented the results of a neutron diffraction experiment using the isotopic substitution technique which gives a direct access to the intermolecular structure of the fluid. These data gave no evidence of the presence of hydrogen bonds in supercritical water, a conclusion at variance with the simulation data and also in contradiction with the spectroscopic data (Raman, IR) collected in the 60's - 70's and mostly ignored in the present day litterature. Very lately new neutron diffraction data are available and do not confirm the first neutron data. In fact, these new data are in reasonable agreement with the prediction of the computer simulations. This point will be discussed in detail as also as can be learn from the simulations on supercritical water.

TALK 11
Monday 12.10 - 12.30

« Water Cluster Anions as the Model of Hydrated Electron. »

Yulia V. Novakovskaya and Nikolai F. Stepanov

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Chair of Physical Chemistry, Department of Chemistry, Moscow State University,
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The state of the excess electron in water and the size of the smallest stable water anion are still not clear.

We optimized the configurations of water cluster anions $(H_2O)_n^-$ with n<8 at the unrestricted Hartree-Fock level with 4-31++G** basis set and without any geometry restrictions. No diffuse functions centered between nuclei of the clusters were added to the basis. The energy characteristics of the anions were calculated in the second order of Moeller-Plesset perturbation theory.

In the anions, the excess electron density is predominantly localized around the hydrogen nuclei, which agrees with experimental data on the s character of the excess electron orbital. The structures of anions can be divided into three groups. In one group, the excess electron density is localized on a molecule that acts as a proton donor in the hydrogen bonds it forms. In the second group, the excess density is localized around four hydrogen nuclei not involved in hydrogen bonds, and the structures are substantially more compact. The third group of structures combines in some way the features of the two former groups. These structures look as if they are composed of two faced chains with the excess electron density localized around four hydrogen nuclei of those two molecules, which face directly each other. The character of the excess electron localization in the anions of the first and second groups can be named surface, while the third group of structures represents what one can refer to as the inner localization.

The vertical energies of detachment of an electron from the anions larger than tetramer are positive, and are sufficiently large for the third group structures.

Varying the exponent of the diffuse s functions centered on the hydrogen nuclei showed the following. When these functions become more diffuse, the energies of the optimal cluster anions of the first and second groups decrease, while those of the third group pass through the minimum, which means that there is an optimum exponent of the s function for the description of the excess electron in water clusters.

The work was financially supported by the Ministry of High School and the Russian Foundation for Basic Research.

TALK 12
Monday 14.00 - 14.30

« Low pressure flame H_2O spectra »

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In room temperature molecular absorption spectra, there is a natural limitation of the accessible range of rotational quantum numbers : just because of the Boltzmann factor, the lower state population of high J transitions is rapidly decreasing as E" is increasing and the corresponding lines become extremely weak.

Testing theoretical models as well as practical applications do, however, press for an extension of the range of rotational quantum numbers. Water vapour is a good example in this respect : when available through experimental measurements, highly excited rotational levels of H_2O represent a benchmark for testing and improving vibration-rotation molecular Hamiltonian models. These are needed to describe the strong centrifugal distorsion effects associated to the large amplitude bending motion of the light hydrogen nuclei. Conversely improved models are used to generate spectroscopic line parameters that can help in the analysis or in the theoretical simulation of high temperature gas phase emission spectra for non intrusive diagnostic or remote sensing measurements.

We present here, from the experimental and spectral analysis point of view, a status of our work performed over the years on high resolution infrared emission flame spectra. Going from ambient pressure flames to low pressure flames is an interesting solution to reduce collision broadening and to produce better resolved spectra. After a brief historical background, a description of the experimental set up, a discussion of the method used to experimentally determine highly excited energy levels and a summary of what has been achieved for H_2O in our group will be presented. Some astrophysical applications will be discussed.

« Excess Electron Interactions with Clusters Composed of Polar, Hydrogen Bond-Forming Molecules: Negative Ion Photoelectron Spectroscopic Studies »

Kit H. Bowen, Jr.

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We will present the results of negative ion photoelectron spectroscopic studies of cluster anions in which excess electrons interact with relatively small clusters composed of polar, hydrogen bond-forming molecules. Water will be given special emphasis. The smallest inorganic cluster species that we have studied are dipole bound dimer anions, such as $(HF)_2^-$, $(H_2O)_2^-$, $(CH_3CN)(H_2O)^-$, $(HCl)(H_2O)^-$, $(HCN)(H_2O)^-$, and (ethylene glycol)$_2^-$. Slightly larger cluster anions which we have studied include trimers, such as $(HF)_3^-$, $(H_2O)_3^-$, $(HCl)(H_2O)_2^-$, $(HCN)(H_2O)_2^-$, and (ethylene glycol)$_3^-$, as well as tetramers, such as $(H_2S)_4^-$. Still larger cluster anions include $(H_2O)_6^-$ and $(H_2O)_7^-$ and their argon solvated cousins, plus $(HCl)(H_2O)_n^-$, with n running up through 7, and $(HCN)_n(H_2O)_m^-$, with n=1,2 and with m running up to over 10. These latter two systems provide clues as to the nature of comparable sizes homogeneous water cluster anions. We will also discuss the solvation of nucleic acid base anions by rare gases and by water molecules. In that work, we see the hydration-induced stabilization of the valence form of the uracil anion.

« TUNNELING DYNAMICS AND SPECTRA OF WATER CLUSTERS »

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and
A. van der Avoird.

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In small cyclic water clusters (trimer, tetramer, and pentamer) one finds two kinds of tunneling processes: hindered rotations of the water monomers about the hydrogen bonds (sometimes called pseudo-rotation or flipping tunneling), and donor (or bifurcation) tunneling, which breaks and reconstructs these hydrogen bonds. With the aid of a rigorously derived model Hamiltonian, which includes also the overall rotation of the cluster, and the use of the permutation-inversion symmetry, we could interpret[1] all the splittings in the measured high-resolution far-infrared spectra of $(H_2O)_3$ and $(D_2O)_3$ and explain the rotational structure in these spectra. Moreover, by means of quantitative calculations on the water dimer and trimer we can test the available water potentials, as well as new potentials from *ab initio* SAPT[2] and from density functional[3] calculations. New results will also be presented for various water trimer isotopomers and for transitions involving vibrationally degenerate energy levels in the cyclic clusters, which display unusual Coriolis coupling effects (joint work with the R. J. Saykally group, University of California at Berkeley).

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« Excitation spectra of intra and intermolecular motions of water clusters »

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We will present experimental investigations of the vibrational motion of neutral water clusters. The OH-stretch spectra are measured by infrared depletion spectroscopy for cluster sizes from n = 7 to n = 10 [1]. The clusters are size selected by momentum transfer in a scattering experiment with a rare gas beam and interact with the light from a tunable OPO system. The experimental results are compared with calculations based on the 3D structures of these clusters. The simplest spectral pattern is found for the cubic octamer. The spectra consists of three groups of lines which can be traced back to different OH groups: the unshifted free, the largely red shifted single donor and the double donor between the other two groups. The other sizes exhibit an increasing complexity by inserting or removing further OH groups. At the low energy end of the spectrum we have measured the intermolecular vibrations by inelastic helium atom scattering [2]. Here a distribution of cluster sizes is probed with varying averaged sizes from n = 11 to n = 200. By accompanying quantum and classical calculations the excited mode near 5.0 meV has been identified as O-O-O bending motion between adjacent hydrogen bonds involving 3-coordinated water molecules on the amorphous surface. The size dependence reveals a lowering of the frequency with decreasing size, in contrast to the results obtained for Ar.

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[2] J. Brudermann, P. Lohbrandt, U. Buck and V. Buch, Phys. Rev. Lett. 80, 2821 (1998)

« Calculation of the water dimer vibration-rotation-tunneling spectrum : Influence of the internal motions »

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The Vibration-Rotation-Tunneling spectrum of the water dimer is first described in the rigid rotor[1] approximation using several potential energy surfaces.

Implementation of the algorithm on a massively parallel computer is also presented.

As none of these surfaces is able to reproduce the experimental data of Saykally and collaborators, the MCY[2] surface has been modified by fitting the calculated energy levels to experiment.

The rigid rotor approximation is then tested within the framework of a Born-Oppenheimer type separation between inter- and intra-modes of the dimer. 12D results show that relaxation of the rigid constraints has very little effect on the VRT spectrum.

[1] C.Leforestier, L.B.Braly, K.Liu, M.J.Elrod and R.J.Saykally, J.Chem.Phys., **106**, 8527(1997).
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TALK 17
Monday 17.00 - 17.30

« Quantum dynamics of the coupled torsional vibrations in water trimer, tetramer and their isotopomers: energy levels, tunneling splittings, and vibrationally averaged rotational constants »

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We have performed quantum three- and four-dimensional model calculations of the coupled low-frequency intermolecular torsional vibrational eigenstates of various isotopic water trimers and tetramers, respectively. In this model, the only allowed internal motions are those of the free O-H bonds constrained to rotate around the hydrogen-bonded O-H bonds of the cyclic trimer and tetramer.

The bound-state calculations employ the ab initio - based modEPEN torsional intermolecular potential energy surfaces and the pointwise discrete variable representation in 3D and 4D. For the trimers, the calculated fundamental excitations have very low frequencies, typically 4-15 cm^{-1}, and are strongly coupled to yield a progression of pseudorotational states delocalized over the sixfold degenerate global minimum. Vibrational averaging of the asymmetric equilibrium trimer structure over the torsional wave funcions is responsible for the experimentally observed oblate symmetric top spectra. For a series of isotopically substituted trimers, we calculate rotational constants vibrationally averaged over the ground and excited torsional eigenstates, which are compared with the available experimental data. In the case of the tetramer, the frequencies of the torsional fundamentals are significantly higher, about 180 and 230 cm^{-1} for $(D_2O)_4$ and $(H_2O)_4$, respectively. The global minimum of the tetramer is doubly degenerate, and the two minima are interconverted by tunneling motion similar to the inversion tunneling in the ammonia molecule.

This inversion motion splits all torsional excitations into pairs of states of opposite parity. At low excitation energies, the torsional motions of the tetramer, unlike those of the trimer, do not couple to give rise to a pseudorotational motion, and the lowest nine levels are not pseudorotational.

At higher vibrational energy, a set of four pseudorotational eigenstates appears.

« Water clusters attached to benzene derivatives: structure, binding energies, ion-chemistry »

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The interaction of water with aromatic molecules is of fundamental importance both in many organic reactions and in the formation of the structure and conformation of many biomolecules. To reduce the complexity of this interaction, we used substituted benzene monomers surrounded by water molecules as model systems. The issues are to get an insight into the molecular parameters determining the strength and the conformational consequences of this solute-solvent interaction and to study the size-specific ion-chemistry of microhydrated aromatic cations.

Infrared-ion-depletion spectroscopy, a double resonance method combining vibrational predissociation with resonant two-photon ionization (R2PI) spectroscopy has been employed to study different substituted benzene$\cdot(H_2O)_n$ clusters with $n < 4$. Benzene, p-difluorobenzene, fluorobenzene, toluene, p-xylene and anisole were used as chromophores in these molecular complexes. From the IR-absorption spectra in the region of the OH-stretch vibrations it could be shown that the water molecules are attached as subclusters to the chromophores. Size and structure of the subclusters could be gained from the IR-depletion spectra. Except in the anisole$\cdot(H_2O)_n$ complexes, where the water clusters form a hydrogen bond to the oxygen atom of the methoxy-group, in all other mixed complexes a π-hydrogen bond is formed between one of the free OH-stretches of the water clusters and the π-system of the chromophore. Characteristic red shifts of this π-hydrogen bonded OH-stretches could be related with atomic charges in the aromatic rings, with the binding strength between the subcluster and the chromophore and with the red-shift of the $S_1 \leftarrow S_0$ transition of the latter. We also observed a cluster-size-selective ion-chemistry depending on the substituent at the benzene ring. With methyl substituents, the ionized chromophore acts as a proton donor, with fluorine atoms, a nucleophilic substitution reaction takes place.

TALK 19
Monday 17.50 - 18.10

« Electronic spectroscopy of phenol(water)$_{1-12}$ clusters: structures and intermolecular vibrations. »

Karl Kleinermanns, Christoph Janzen, Daniel Spangenberg, Wolfgang Roth, Michael Schmitt and Markus Gerhards

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The structures and intermolecular vibrations of jet cooled phenol(H_2O)$_n$ were investigated in the electronic ground state by dispersed fluorescence and in the electronically excited S_1- state by mass resolved resonant 2-color/2-photon ionization, spectral hole burning and rotationally resolved laser induced fluorescence. Vibronic spectra up to a cluster size of n=12 could be taken via excitation just above the ionization thresholds and were discriminated for isomers via hole burning.

The measured rotational constants, the analysis of the (electronic) spectral shifts and ionization potentials and the comparison of measured and *ab initio* calculated intermolecular vibrations are used to determine the structures of these two-, three- and (partially) tetracoordinated H-bridge systems.

The n=1 cluster exhibits a *trans-linear* hydrogen bond. The aggregates with n=2-4 H_2O are cyclic H-bridged systems with single H-donor units, whereas double H-donor H_2O presumably form a cage structure in case of n=5. The vibronic spectra of the n=8 and n=12 cluster in the spectral region of the n=1 cluster are especially prominent. The experimental data point to H-bridge association of phenol to cube like (H_2O)$_8$- and (H_2O)$_{12}$- clusters exhibiting the tendency of a particularly high cluster stability for a maximum number of planar (H_2O)$_4$- rings. Another n=8 isomer shows a very intense vibronic spectrum with absorption near to the n=4 spectrum. The spectral shift points to a structure with (H_2O)$_4$ associated to the water molecules of the cyclic phenol(H_2O)$_4$ (« cube with handle » structure). Another intense vibronic spectrum was observed on the n=7 mass trace with a small blue shift relative to the n=3 cluster absorption. The spectral shift points to a cube structure with (H_2O)$_4$ association to phenol(H_2O)$_3$.

The investigations show the importance of the intermolecular stretch vibrations and mutual vibrational motions of the phenyl ring and the water network as well as the red- and blue shifts of the electronic spectra for structural analysis.

TUESDAY

TALK 20
Tuesday 9.30 - 10.00

« First principle calculation of spectrum of hot water »

Jonathan Tennyson

University College London

The infrared spectrum of water is probably the most intensely studied of all molecules and yet much of it remains poorly understood. Full variational solutions of the problem which go beyond the standard Born-Oppenheimer approximation are used to give vibration-rotation quantum number assignments for individual lines. Using this method we have successfully analysed spectra from a variety of observations.

However there remains considerable work to be done. For instance our analysis of highly congested infrared absorption spectra recorded in sunspots [1] (T ~3000 C and up to 50 spectral lines per cm-1) has so far only assigned 15% of the transitions in some regions. Improvements to the theory involve inclusion of relativistic effects in the electronic structure calculations and the inclusion of further non-Born-Oppenheimer terms in the calculations. Progress on this work, and comparisons with similar calculations on H3+, will be presented at the conference. Methods for calculating ALL the bound states of water will also be mentioned.

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TALK 21
Tuesday 10.00 - 10.30

« Analysis of hot water spectra in sunspots and the laboratory »

Oleg L. Polyansky

(University College London)

We have solved the problem of water line assignment using non-perturbative, first principles calculations. This method is general and can be applied not only to water, but to many other triatomic molecules.

Many thousands of water lines have been observed experimentally and remained unassigned for a decade or more. We have assigned them in the most formidable regions of high rotational and high vibrational excitation. So far we have assigned 13 000 new water lines from 300 to 25 000 cm^{-1}. We did this analysing infrared spectra recorded in absorption in sunspots, and in emission in the laboratory, and in cold laboratory spectra in the optical and UV regions. Our assignments have doubled both the range and number of observed energy levels. We have also seen many vibrational bands for the first time.

« Evaluation of Water Vapor Line-parameter Databases: HITRAN and HITEMP »

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and

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The HITRAN molecular spectroscopic database[1] has been the international standard for providing the necessary fundamental spectroscopic parameters for diverse terrestrial atmospheric transmission and radiance calculations since its publication in 1973. Water vapor was historically the "first" molecule on this database, and the parameters (line position, intensity, halfwidths, lower-state energy, etc) have been periodically updated. HITRAN was designed for temperatures and attenuation consistent with terrestrial applications. A new analogous database, HITEMP, has been initiated to satisfy the requirements of higher temperature applications. This has required different treatments of the Hamiltonian than was necessary for HITRAN.[2]

Comparisons at the standard temperature (296K) and 1000K are shown of the spectra obtained for water vapor between HITRAN, HITEMP, and the line-list of Partridge and Schwenke.[3]

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2. R.B. Wattson and L.S. Rothman, "Direct Numerical Diagonalization: Wave of the Future," *JQSRT* **48,** 763 (1992).
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TALK 23
Tuesday 11.30 - 12.00

« The photodissociation of water in the first absorption band: A prototype for fast and direct fragmentation »

Reinhard Schinke

Max Planck Institüt für Strömungsforschung, Göttingen, Germany.

We will discuss the photodissociation of water in the first absorption band ($\tilde{X}\ ^1A_1 \rightarrow \tilde{A}\ ^1B_1$), which is an prototype of very fast and direct fragmentation on a three-dimensional potential energy surface.[1] It is the first dissociation process that was theoretically studied in full dimensionality on an accurate potential energy surface and much was learnt about photofragmentation in general.[2] The comparison with very detailed experimental data is unprecedented. We will highlight the absorption spectrum, the very weak diffuse vibrational structures, and the final state distributions of the OH fragment and their relation to the topography of the potential surface. Some results of similar molecules -H_2S and O_3- will also be presented in order to underline the similarities and the differences. In addition, we will speculate about the possibility of the $\tilde{X}\ ^1A_1 \rightarrow {}^3B_1$ singlet-triplet transition, in order to (possibly) explain some totally unexpected experimental results concerning the H/D branching ratio in the dissociation of HOD, which were recently obtained by Nesbitt and coworkers in the dissociation at 193 nm.

References

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« Ab initio dynamic multipole polarizabilities and hyperpolarizabilities of H_2O and the long-range interaction coefficients for its dimer »

***Wilfried Meyer* and Dirk Spelsberg**

Fachbereich Chemie, University of Kaiserslautern, Germany

Perturbed states representing the response to an external electric field are obtained from multi-reference configuration interaction wavefunctions. The multi-configurational reference function is designed to represent the ground state as well as the perturbed and even the first excited states on equal footing, i.e. orbital optimization is performed in a perturbed multi-reference self-consistent field procedure. For various perturbing operators, several perturbed wavefunctions for different frequencies of the perturbing field are obtained simultaneously with the corresponding lowest excited state. From these sets of perturbed and excited states, reduced spetra are derived which represent effective oscillator strength distributions and serve to calculate dynamic polarizabilities for the frequency range up to the first excitation energy. The related dynamic hyperpolarizabilities and orientation-dependent longe-range interaction coefficients are also derived. The results for both the dynamic polarizabilities and the interaction coefficients are found to be in excellent agreement with available experimental data and other accurate theoretical values. The calculations of oscillator strength distributions for the entire relevant frequency range will be discussed.

TALK 25
Tuesday 14.00 - 14.30

« Breaking bonds in water and water clusters: zero point and vibrationally mediated photofragmentation dynamics »

Ondrej Votava, Tanya Myers, David F. Plusquellic and David. J. Nesbitt

JILA, University of Colorado
National Institute of Standards and Technology
and
Department of Chemistry and Biochemistry
University of Colorado
Boulder, CO 80309

This talk will discuss ongoing projects in high resolution IR and IR/UV dynamics of both water and water containing complexes, with a focus toward providing fully rigorous comparison with exact quantum theoretical calculations on trial potential surfaces. Time permitting, the topics address recent progress in the following areas: 1) Single mode, near IR light from a injection seeded optical parametric oscillator has been used to investigate vOH=4-0 and 3-0 overtone spectra of HOD. The body fixed alignment of the transition dipole moment is measured via a/b-type intensity ratios, which is found to systematically rotate away from the OH bond with increasing quanta of excitation. This is in disagreement with simple bond dipole models but in good agreement with recent dipole moment surface predictions. 2) High resolution spectroscopy of H_2/D_2-H_2O clusters has been characterized in the HOH bending region with diode laser direct absorption methods, which clearly identify the role of large amplitude motion and yet also the propensity of H_2O to act as a "proton acceptor" in a near C_{2v} vibrationally averaged geometry. 3) Isotopic photofragmentation studies of jet cooled H_2O, HOD and D_2O at 193 nm have been performed to investigate bond breaking dynamics from far-off resonance photolysis in the extreme non-Franck-Condon regime. The results indicate a 12-fold propensity to cleave the OH vs OD bond, which, though in good qualitative agreement with a picture of vibrationally mediated photolysis via isotopically sensitive zero point motion, is more than an order of magnitude overpredicted by exact quantum calculations by Schinke and coworkers. 4) Triple resonance IR/UV/UV studies with single mode OPO's are used to investigate vibrationally mediated photofragmentation dynamics in quantum state selected clusters. Work on Ar-H_2O and Ar-HOD clusters will be addressed, as well as recent progress in other M-H_2O clusters.

« SOLVATION EFFECTS ON REACTIONS IN CLUSTERS »

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Recently, we have focused attention on studies of the influence of degree of clustering on the uptake of several acid molecules into aqueous systems. We expect that our findings will be of interest in comparison to various theoretical computations bearing on the formation of ion pairs upon solvation, as well as the adsorption of acid molecules onto ice-like or aqueous surfaces. In addition, we believe that our results will be of value in providing further insight into open questions in the field of atmospheric chemistry pertaining to heterogeneous processes involving ice crystals and cloud particles.

In this talk, results will be presented on reactions of HNO_3, HBr and HCl with water clusters, where major attention will be devoted to the last system. In recent work on HCl, we have found that a minimum of 9 water molecules bound to a hydronium ion is required for the dissolution of one HCl, 12 for two, 18 for three, and 24 for four HCl's. This pattern is consistent with some theoretical calculations which suggest that the formation of ion pairs takes place at a water to HCl ratio of six to one.

Another interesting and revealing finding has emerged from our recent studies of the subsequent uptakes and their pressure dependence. The study has shown that water clusters of size smaller than nine do not take up an HCl, but once one HCl is incorporated through dissolution, an association reaction enables a second HCl to be taken up without direct dissolution into an ion pair. Similar observations are found for all of the subsequent addition steps showing two distinct HCl types, one an adsorbed species and the other a dissolved acid molecule. In order to further elucidate the nature of HCl-water interactions, and the ensuing reactions involved in solvation, femtosecond pump-probe experiments were undertaken. Results of recent experiments will be presented and discussed.

TALK 27
Tuesday 15.00 - 15.30

« Ab initio calculations of water line strengths »

David W. Schwenke and Harry Partridge

NASA Ames Research Center, Moffett Field, CA 94035-1000

In 1996 [J. Chem. Phys. **106**, 4618 (1997)] we determined high quality ab initio potential energy surface (PES) and dipole moment function for water. After making small empirical adjustments to the PES, we could obtain excellent agreement with experimental line positions as given in the HITRAN~96 data base: the 10, 25, 50, 75, and 90 percentiles of the difference between the calculated and tabulated line positions are -0.11, -0.04, -0.01, 0.02, and 0.07 1/cm. Based on our results, it appears that about 3% of the tabulated experimental line positions are incorrect. To obtain results of similar quality for other hydrogen isotopes, a small mass dependent correction is required for the PES. Using the adjusted PES and ab initio DMF, we computed a high temperature line list consisting of nearly 400 million lines. In this talk we will set the stage and discuss the questions raised in our work, and the answers obtained to date.

« Reactivity of charged water clusters »

Gereon Niedner-Schatteburg

Institut für Physikalische und Theoretische Chemie
Technische Universität München, 85747 Garching, Germany

By means of a high resolution Fourier-Transform-Ion-Cyclotron-Resonance (FT-ICR) ion trap we have investigated the bimolecular reactivity of various cationic and anionic water clusters $X^{\pm}(H_2O)_n$, $n \leq 100$ with selected inorganic and organic compounds [1-9]. The clusters were found to act as microscopic solvent droplets and according to «text book» chemistry. Their investigation, however, allows for an in detail insight into elementary steps of these reactions of either applied or fundamental interest. Concomitant fragmentation of stored water cluster ions due to absorption of black body radiation [5,7] helps to remove solvent molecules step by step and to study solvation effects as a function of cluster size. Numerous future investigations are foreseeable.

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TALK 29
Tuesday 16.20 - 16.50

« GENERATING FUNCTION MODEL FOR CALCULATION OF HIGH RESOLUTION SPECTRA OF Ti WATER MOLECULE »

Vi.G.Tyuterev, S.N.Tashkun'* and S.N.Mikhailenko***

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****LTS, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055, Akademicheskii 1 , Tomsk, Russia**

Applications of the generating function model [1 -3] are considered for a fitting of high rotational levels of water molecule in the domain of rotational quantum numbers where the standard expansion of effective rotational Hamiltonian has a slow rate of convergence or diverges. This model is derived by taking into account of the most important part of the bending-rotational interaction in the zero-order approximation and is equivalent to a partial summation of centrifugal distortion corrections up to infinite order of the perturbation theory. Typically it provides a considerable improvement in the standard deviation of fit and especially in extrapolations compared to conventional effective Hanitonians as it has more realistic asymptotic behaviour. It allows one to easily determine « radii of convergence » for the usual power series expansions of the centrifugal distortion operator. Comparisons with global calculations based on accurate potential functions and applications to assignment of high-resolution spectra [4] will be discussed.

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TALK 30
Tuesday 16.50 - 17.20

"Charge Transfer Dynamics in Aqueous Cluster Systems and the Reassessment of Fundamental Properties of Water through Cluster Studies",

James V. Coe

Department of Chemistry, the Ohio State University, Columbus Ohio, 43210-1173, USA

This talk will be presented in two parts. The first part involves investigations from a variety of groups using aqueous clusters which have been combined to produce major reassessments of fundamental properties associated with bulk water. The connection to bulk of cluster based results on hydrated electrons and ions will be presented providing reassessed values of the band gap of water, the liquid electron affinity of water, and the absolute hydration free energy and enthalpy of the proton. The generalized trends toward bulk in the clustering energetics of both neutral and ion solvated clusters will also be discussed. In the second part of the talk, experimental results on the charge transfer dynamics of ion systems associated with water will be presented. The effect of clustering water molecules about the reactants of the ion-ion recombination reaction, H_3O^++OH^-, and a new method to study the fast neutral products of dissociative charge transfer interactions of $H_3O^+(H_2O)_n$ in an ion beam with Ar in a collision cell will be discussed. Both results pertain to the fate of the various electronic states of the H_3O Rydberg radical which will also be discussed in the context of electron recombination with H_3O^+.

TALK 31
Tuesday 17.20 - 17.40

« Vibrational predissociation spectroscopy of negatively charged water clusters and hydrated halide ions: Making and breaking the inter-water hydrogen bonds »

Patrick Ayotte, Gary H. Weddle, Jun Kim, and Mark A. Johnson,

Sterling Chemistry Laboratory, Yale University, New Haven, CT 06520

We report the morphology of the water networks adopted in several charged systems with an increasingly delocalized negative charge cloud. The key to our method is to first embed the hydrate into a large cluster of (up to 15) argon atoms, and then record the infrared spectrum of mass selected species inside the clusters via predissociation of the argon "matrix." This technique has the two major advantages of cooling the ion complexes as well as quenching rotational structure to cleanly reveal vibrational band origins. We report the evolution of the water network down the halide series, $X^-(H_2O)_n$ [X = Cl, Br, I; n = 1-3], where the general trend is that the water subcluster becomes more tightly bound as the ion-water bond is weakening, in general agreement with ab initio calculations. All of the trimers adopt very symmetrical arrangements involving a cyclic water trimer with equivalent water molecules. We then sequentially warm the clusters to observe the water subcluster break up into single water molecules orbiting the ion.

The negatively charged water clusters, $(H_2O)_n^-$, where the excess electron is contained in a very diffuse orbital, display a very different motif, whose characteristic spectrum persists throughout the small clusters. With the help of calculations provided by Prof. K. D. Jordan to interpret the dependence of the bands on isotopic substitution, we conclude that trend these clusters occur with a *linear* water backbone where the resulting large dipole moment binds the excess electron.

TALK 32
Tuesday 17.40 - 18.00

« The spectroscopy and dynamics of water solvation in small biomolecule(water)$_n$ clusters »

J.R. Carney, C.J. Gruenloh, F.C. Hagemeister, and T. S. Zwier

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Gas phase clusters containing water are currently being used as an important testing ground for existing intermolecular potentials for water, both in the presence and absence of solutes. One of the particular experimental challenges to be overcome in such studies is the exponentiating number of conformational isomers which can be present in such H-bonded aggregates. When one or more molecules in the cluster can be resonantly ionized, a combination of resonant multiphoton ionization and hole-burning methods can often be used to sort out the ultraviolet spectrum of each size and conformation cluster. The double-resonance method of resonant ion-dip infrared spectroscopy (RIDIRS) can then be used to record each cluster's hydride stretch infrared spectrum free from interference from others present in the expansion. The sensitivity of the hydride stretch region to the number, type, and strength of hydrogen bonds present make it a particularly powerful probe of the H-bonding topologies of the clusters. When benzene is used as aromatic chromophore, it serves as a surface-attached probe molecule for the (water)n cluster. Other aromatics, such as indole, N-methyl-indole, tropolone, and pyridone, have H-bonding sites which can serve as attachment points for water molecules. Examples will be taken from each to demonstrate the rich diversity of structural types taken up by water clusters in these contexts, emphasizing the spectroscopic signatures which each structure produces. The crucial role played by theoretical calculations in assigning spectra to unique H-bonding topologies will also be stressed.

WEDNESDAY

« H_2O^+ in Comets »

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Ionized water vapor is an important tracer of the photochemistry in the ion tails of comets.[1] It derives from the most abundant condensed volatile in comets, frozen water, and, through detailed modeling of the chemistry of cometary comae, its abundance relative to other ion fragments can be used to distinguish which of the possible carbon-bearing molecules, CO or CO_2, dominates in the primordial ice.[2,3,4] Studies of the absolute production rates of H_2O^+ in cometary comae, also made possible through detailed chemical models, show promise as a predictor production rate of H_2O gas.[5]

The laboratory isolation[6,7] of the spectrum of H_2O^+ and its identification[8,9] in the spectrum of comet Kohoutek occurred nearly simultaneously only 25 years ago. Initial studies[1] quickly established that resonance fluorescence was the dominant excitation mechanism which led to the emission observed in comet Kohoutek, but they were unable to establish which ionization process dominated the production of H_2O^+.

In the years since these pioneering discoveries, no new quantitative measurements of H_2O^+ emissions were reported until ground-based observations of comets P/Giacobini-Zinner[10], P/Halley[4,11] and Bradfield[4] were published. The analyses of these new data were based on improved fluorescence efficiency factors,[11,12] but comparisons with spacecraft *in situ* measurements of H_2O^+ abundances showed unexplained differences.[4,10,11]

Similarly, significant advances were made in the modeling of cometary comae,[2,3] during this period. And, recently, a study[5] of H_2O^+, using a multiscale MHD model to describe the ion chemistry, successfully described the spatial distribution of H_2O^+ observed for comet P/Halley,[11] and identified photoionization and electron ionization of H_2O as the major production process for H_2O^+. However, the agreement could be obtained only if the fluorescence efficiency factors, or g-factors, for the ionized water vapor bands were decreased by a factor of two. Such an ad hoc revision of the g-factors also brings the ground-based and *in situ* measurements for comets P/Giacobini-Zinner and P/Halley into agreement.[11]

The physical basis[13] for this revision, which had not been recognized in the recalulations[11,12] of the g-factors, is that the odd-$\upsilon_2' - 0$ vibrational bands are comprised of only Σ and Δ sub-bands, while the even-$\upsilon_2' - 0$ vibrational bands are comprised of only Π sub-bands, because of nuclear symmetry. Consequently they sample different lower rotational levels, and the factor of two applied to any one band compensates for the population in unsampled rotational levels. However, this approach works only if the rotational temperature is sufficiently high to populate both sets of rotational levels equally. However, temperatures are not always high enough to equilibrate these levels.[9] A better approach is to sum the results from a pair of even- and odd-υ_2' observations, using the existing values for the g-factors.

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TALK 34
Wednesday 10.00 - 10.30

« Structure and Spectroscopy of Water Cluster Anions »

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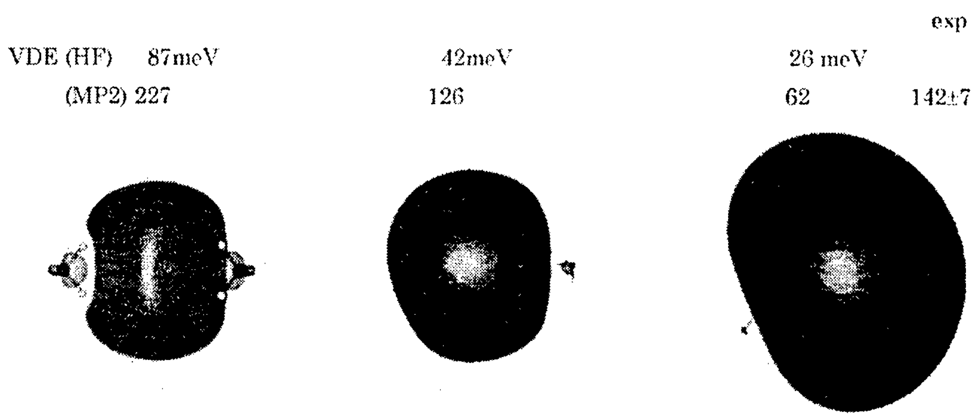
Since the first observation of the water cluster anions in the gas phase, many experimental and theoretical works have been reported. In the experimental studies, water cluster anions, $(H_2O)_n^-$, n ≥ 2, can be found in mass spectra. Interestingly, the observed signals for n = 3, 4, 5, 8, 9 and 10 are very weak. In the theoretical point of view, two types of structures have been discussed for these anions. One is the internal state, in which the excess electron is localized inside the cluster. Another is the surface state, in which the excess electron is bound to the electrostatic dipole field of the water clusters, the latter being called dipole bound. It has been believed that small cluster anions have a dipole-bound excess electron. Recently, however, we have found a stable dimer anion in which an excess electron is confined in two water molecules facing each other [1]. A large basis set and the electron correlation at least MP2 level are required. The basis set used is 6-311++G** + 7sp, where even tempered seven s and p functions are placed at an optimized center. We have extended the study for trimers, and found two isomers of internal type as well as the dipole bound anion recently reported [2]. The basis set superposition error was carefully examined. In the figure below, 50% of the excess electron is contained inside of the boundary. In terms of total energy, the dipole bound anion (far-right in the figure) is the most stable because of the hydrogen bonds. On the other hand, the vertical detachment energy (VDE) is the smallest among three anions. The anion of D3h symmetry (far-left in the figure) has the largest VDE, and is the smallest in size.



« STUDY OF HIGHLY EXCITED STATES OF WATER ISOTOPOMERS IN TOMSK »

A. D. Bykov, L. N. Sinitsa

Institute of Atmospheric Optics, Tomsk, Russia

Highly excited vibrational states of H_2O-16, H_2O-17, H_2O-18, HOD and D_2O have been studied using highly sensitive laser spectrometers. Intracavity laser spectrometers and opto-acoustic spectrometers operate in 8000...17000 cm^{-1} spectral region and have threshold sensitivity to absorption about 10-8 cm^{-1}. The spectra were recorded at low and high temperature up to 900 K. Comprehensive analysis of the spectra recorded using laser spectrometers and using the FT spectrometers with long absorption path have been performed.

The spectra contain many weak bands, high-J transitions and hot bands. These spectra are congested and one should expect to find a lot of different variants of assignment. The special method was used to make the reliable line identification. The pattern recognition theory was used for line assignment, it allowed one to facilitate the analysis and create the special expert system for the automatic spectrum analysis. The line assignment used iterative procedure when spectroscopic parameters of the investigated states were determined during every step of the assignment and accurate predictive calculations of line positions and strengths were fulfilled fornew J-levels.

Highly excited states were found in the spectra and analysed :

H_2O-16 (070), (040) (051);
H_2O-17 (220), (022);
H_2O-18 (051), (070);
HOD (500), (050), (051), (005);
D_2O (130), (031), (030);

The analysis of the vibration-rotation spectra of water molecule in near infrared and visible regions requires modification of the Effective Hamiltonian theory. Effective Rotational Hamiltonian approach uses the perturbation theory expansions and these series are divergent at large values of rotational quantum numbers. Dealing with the problem of excited states of the light nonrigid molecules one should try to find the approach which is able to account for the possible divergence of the perturbation theory series, but still keep an idea of Effective Hamiltonians to provide easy handling of experimental data. The modification of Effective Hamiltonian approach was made with the use of divergent series summation methods.

Typical scheme of polyads of interacting states in high frequency range is destroyed by unusual resonance perturbations with "dark state". It was found that strong bending-rotation interaction in the H_2O molecule leads to a new type of resonance (HEL - resonance) which couples the vibrational states formally belonging to different resonance polyads.

Water vapor line shifts induced by pressure were studied for the H_2O-16 overtones. The dependence of line shift coefficients on the vibrational and rotational quantum numbers was explained.

The research was made possible in part by Grant No 98-33-33801 from RussianFoundation of Basic Research.

TALK 36
Wednesday 11.30 - 11.50

« Interplay between Cooperativity and Hydrogen Bonding Network in Water Clusters »

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Clusters of water molecules are held together by hydrogen bonding networks. These networks are differentiated by the participation of the individual water molecules in the hydrogen bonds either as proton donors (d), proton acceptors (a) or their combinations. It has long been assumed that the stability of clusters is determined by the dominant two-body interactions between the water molecules. We have found that homodromic hydrogen bonding networks, i.e. those exhibiting donor-acceptor (da) arrangements between all water molecules, are associated with the largest non-additivities among other networks present in low lying minima of water clusters. Among the non-additive terms, three-body terms are mainly responsible for determining the relative stabilities between the various trimer through pentamer isomers.

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TALK 37
Wednesday 11.50 - 12.10

« Structure, Intermolecular Dynamics, and Binding Energy of Organic Molecule-Water Complexes »

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Structural and energetic data of gas phase clusters are important for the understanding of the intermolecular interaction of water with aromatic molecules on a microscopic scale. Here we present new results on the structure, intermolecular dynamics, and dissociation energy of clusters of water with molecules ranging from phenol to the amino acid chromophor indole (C_8H_7N).

Highly resolved sub-Doppler spectra have been measured with rotational resolution by mass selective resonance-enhanced two-photon ionization. The first photon originates from a nearly Fourier-transform limited laser pulse with a frequency width of typically 70 MHz in the UV. The pulses are produced by pulsed amplification of cw single mode dye laser light and frequency doubling. To analyze the complex rotational structure in the vibronic bands of the clusters we developed a new automated fitting procedure yielding accurate values for the rotational constants by optimization of the crosscorrelation of a theoretical spectrum with the experimental spectrum (Correlation Automated Rotational Fitting: CARF[1]). Fitting of the rotational constants is possible without a preceding analysis and assignment of the rotational transitions. We present results for the structures of benzonitrile-water and indole-water, and the intermolecular dynamics of hydrogen bonding in phenol-water. In benzonitrile-water ($C_6H_5CN.H_2O$) the water is found with its oxygen nearly in the plane of benzonitrile, nested between the cyano group and the ortho hydrogen[2]. In indole-water the water is in a hydrogen accepting position attached to the amino hydrogen with its oxygen oriented towards the NH hydrogen[3]. In phenol-water ($C_6H_5OH.H_2O$), we investigated the intermolecular dynamics by high resolution spectroscopy[4] . An autocorrelation procedure of the higlhly resolved vibronic bands yields directly the torsional splitting of the individual vibronic bands prior to a rotational analysis. In this way we were able to assign several intermolecular vibrational states and investigate the tunnel splittings caused by the hindered rotation of the water moiety.

Mass analyzed pulsed field threshold ionization (MATI) of optically excited high Rydberg states is a new method for the production of vibrational state-selected molecular and cluster ions. Its mass selectivity allows us to detect the threshold for cluster dissociation with high precision[5]: At the dissociation energy the tlareshold ion signal at the parent mass breaks down and at the same time threshold ion signal appears at the fragment mass. Recently we were able to measure the first threshold ion spectrum of a complex with water and hydrogen bonding: indole-water[6]. The so determined large binding energy, Do=1630 cm^{-1}, of the neutral indole-water complex and Eo=4790 cm^{-1} of the ionic cluster supports the structural data found from high resolution spectroscopy and points to a hydrogen bonding between the hydrogen-donating indole and the oxygen atom of the water molecule. Furthermore, energetic data obtained with the MATI techniqne for the phenol-water complex are presented.

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« Water vapor in the atmosphere : radiative effects and role on the climate system »

Michel Desbois

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Water is a fundamental element of the climate system of the Earth, not only because the water cycle is the most sensible element of climate, but also because water plays a major role in the radiative budget of the planet. The greenhouse effect of the atmospheric water vapour is the most important among the components of the atmosphere, and preserves in itself our planet from freezing. But the water vapour amount in the atmosphere is very variable in space and time, depending on many thermodynamic and dynamic processes. For example, the vertical distribution of this constituent is very important for the strength of its greenhouse effect, and the mechanisms which are responsible for this distribution (which occur at a very large range of scales) are still unsufficiently known to allow us to predict the "water vapour feedback" on climate change processes.

Another major effect of water on the radiative budget of the Earth is due to the presence of clouds, constituted by liquid or solid water particles. Clouds reflect part of incident solar radiation reaching our planet (albedo effect), but also act for greenhouse effect as they block part of the Infrared radiation emitted by the Earth surface. These two effects can compensate or one can dominate the other, depending of the type of cloud (globally, the albedo effect seems to dominate). The problem of radiative transfer, absorption-emission and diffusion by clouds is complicated by the bad knowledge of the distribution of sizes (and shapes, specially for crystals) of the cloud particles. Moreover, the geometry of the clouds themselves may have a role on the radiative transfer. Recently, a phenomenon known as "the anomalous cloud absorption" was shown up by several measurement campaigns. The reason of this phenomenon, which woul have a great impact in our knowledge (and representation in models) of the energetic budget of a cloudy atmosphere, and its effect on surface radiation, has not been clearly identified up to now.

The last energetic effect of atmospheric water related to climate is the release of latent heat when the water coming from evaporation at the surface of oceans and lands condenses in clouds. In fact, the latent heat release is significant mostly for the rain-producing clouds, where much more water condenses, in a continuous way (the water is evacuated by precipitation) than in non precipitating clouds, which have a limited liquid water content, and where condensation is compensated by evaporation.

Finally, the question of the water vapour in the stratosphere, although it has less direct energetic effects, due to the small quantities present, can also be significant for some climate processes including chemical and photochemical reactions. The "Ozone hole" noticed over the polar region is depending on processes including water vapour. The repartition of the water vapour in the stratosphere is also indicative of dynamical processes related to different kinds of waves of this region.

The observation of atmospheric water vapour and clouds from the surface of the Earth is neither enough precise, nor sufficiently continuous in space and time to provide useful information for climate and climate processes purposes. Moreover, water vapour effects are pertubating the satellite measurements of other geophysical atmospheric or surface parameters. Therefore, a number of satellite systems have been set up to provide radiative measurements related to water vapour and clouds.

Putting aside the problem of cloud observation, which is a big subject per se for meteorologists and climatologists, the retrieval of water vapour from space measurements takes into account the radiative properties of water vapour. Different techniques are used

as well for measuring the integrated amount of water vapour as for attempting to retrieve its vertical distribution.

One of the first use of meteorological satellites was to derive sea surface temperature from measurements in "infrared windows" of the absorption spectrum of the atmosphere (f.e. 10-12 μm). In order to correct for water vapour absorption effects, one splits this window into two parts (split window technique) where the absorption by water vapour is slightly different. This differential technique allows to correct for the water vapour total absorption along the path. The same kind of technique can be applied using two different sights (on vertical, one slanted) of the same point of the sea surface in the same IR window, leading to different pathlengthes in the atmosphere. Same approach can be applied in the VIS domain, when looking at high albedo surfaces and measuring differential absorption. However, these differential techniques, even though they permit the requested corrections, are often not precise enough for retrieving total amount of water vapour. Problems of other absorbing objects in the window (volcanic ashes, for example) or inapropriate accounting of water vapour absorbing properties (continuum) may cause some trouble.

The total water vapour content determination (over oceans) made a big progress with the use of microwave radiometers, which are less sensible to other constituents of the atmosphere (clouds, dust,...). These instruments are now operational on different satellites, including in conjunction with altimeters of the sea surface, which need to correct for water vapour amount. Their results are considered satisfactory for the atmospheric community needs.

Concerning the vertical distribution of water vapour, the principle is to use "sounding" channels, taken more or less close to maxima of absorption of water vapour. The radiation arriving to the satellite comes from more or less deep layers of the atmosphere depending on the absorption of the chosen channel. The most common channels used for this retrieval, in the IR domain, are in the absorption band around 6.7 μm, while in the microwave domain, the band near 183 Ghz is more and more used, with the aim to be less penalized by clouds and high water vapour contents, specially in the tropical areas. The problem of restituting the water vapour profile is complicated by the need of a preliminary restitution of the temperature profile (using CO_2 IR band near 15 μm, and/or microwave oxygen absorption near 50 GHz), by the contribution of surface in some channels, and by the not very sharp shape of the contribution functions (the range of altitude levels contributing to the radiance measured in a particular channel is wide). Precise knowledge of the properties of the water vapour spectrum is also required. In practice, direct calculations of radiances from a representative data bank of atmospheric profiles are performed. True radiances are then compared to the simulated ones, allowing a choice in the bank of simulated data. Neural network techniques are more and more used to perform the inversion. Another approach consists in assimilating directly measured radiances in atmospheric general circulation models (which are also able to simulate observed radiances). There is presently good hope that this last approach will lead to a better description of the general water vapour distribution by models, contributing both to better weather forecasts and to better climatologic data.

However, the level discrimination problem with the passive sounding techniques will never be overcomed. In this domain, active techniques using lidars are more promizing. Differential absorption lidars, for example, can measure water vapour absorption for precise depths of atmosphere, but they are still experimental, and have to be developped for space applications.

TALK 39
Wednesday 14.00 - 14.20

« Local Treatment of Electron Correlation in water clusters »

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The structures and stabilities of small water clusters $(H_2O)_n$, n=1..6 are studied with local electron correlation methods. It is demonstrated that the local treatment eliminates basis set superposition errors (BSSE), which constitute a major problem for supermolecular calculations on intramolecular complexes and clusters, to a large extent. Furthermore, analytic gradients for local second-order Möller-Plesset perturbation theory (LMP2), which are not more expensive than ordinary (canonical) MP2 gradients, offer a new and inexpensive route to BSSE free cluster geometries.

Results for various basis sets are presented which show that the interaction energies and structural parameters obtained by LMP2 without counterpoise correction are in close agreement with counterpoise corrected conventional MP2 results. The local concept also allows for a partitioning of the interaction energy into different excitation classes (intramolecular-, ionic-, dispersive contributions). These contributions can be related to results from symmetry adapted perturbation theory and provide further insight into the nature of the weak forces acting between the molcules in such clusters.

TALK 40
Wednesday 14.20 - 14.40

« Quantum Simulation of the Methanol-Water Complex »

J.L.Iosue, D.M.Benoit and D.C.Clary,

University College London, London, UK

We use diffusion quantum Monte Carlo methods in a theoretical investigation of the van der Waals complex formed between water and methanol. As both molecules are capable of acting as either proton-donor or proton-acceptor, two distinct structures are possible for the dimer: a methanol donor form, $CH_3O\text{-}H\cdots OH_2$, and a water donor form, $CH_3HO\cdots H\text{-}OH$. Due to the small energy difference between them, there has been some uncertainty in characterising the strongest bound conformation. To date, both experimental and computational results vary, and current spectroscopic methods have been unable to observe both structures. Vibrationally averaged structures, bond energies and rotational constants for the two structures and several isotopomers of $CH_3OH\cdots\cdots H_2O$ will be presented and compared to the latest experimental results in an attempt to determine the lower-energy conformation and relative stability.

TALK 41
Wednesday 14.40 - 15.00

« THE INFRARED SPECTROSCOPY AND DYNAMICS OF WATER CLUSTERS »

Roger Miller

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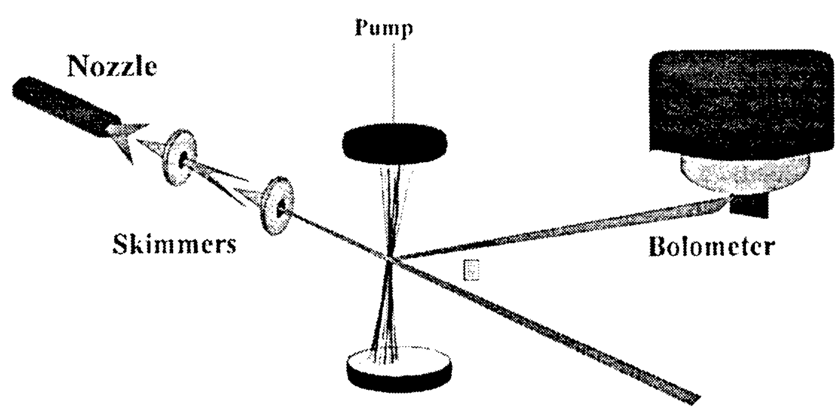
Chapel Hill, N.C. 27599

The optothermal detection method has been used to obtain high resolution near infrared spectra of a number of water complexes that show interesting vibrational dynamics. Of particular interest is the N_2-H_2O complex in which both the water and nitrogen molecules undergo tunneling. The near infrared spectrum of this complex provides information on the associated tunneling frequencies and their dependence on the intramolecular vibrational state. The vibrational predissociation of isotopically substituted acetylene-water will also be discussed.

Preliminary results will also be reported for the state-to-state vibrational predissociation of the water dimer. These experiments are carried out by pumping the parent complex to an O-H vibrationally excited state, whereupon vibrational predissociation results in the production of two water molecule fragments that recoil from the molecular beam. The resulting photofragment angular distributions have been recorded and will be discussed.



Experimental Apparatus used for measuring the photofragment angular distributions resulting from vibrational predissociation of weakly bound water complexes.

TALK 42
Wednesday 15.00 - 15.20

« Acid Ionized HBr in a Four-Water Cluster »

Bradley J. Gertner and James T. Hynes

Department of Chemistry and Biochemistry
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In addition to its interest as a fundamental and important chemical reaction, the acid ionization — the proton transfer to a water molecule — of hydrogen halides in water is of environmental significance. Just as the acid ionization of HCl at the surface of ice is a key ingredient in the heterogeneous chemistry on polar stratospheric cloud particles in Antarctic ozone depletion mechanisms [1, 2], the acid ionization of HBr at the surface of ice plays an essential role in Arctic region atmospheric heterogeneous ozone depletion mechanisms [3].

In preparation for a theoretical study of the condensed phase reaction of HBr on ice, we have undertaken extensive quantum chemical studies [at the electron correlated MP2/6-31+G(dp) level of theory, and specially optimized variants thereof] of this molecule in small water clusters. In this talk, we will focus on the finding [4] that HBr is already acid-ionized in a cluster of as few as four water molecules. The structure of the H_3O^+ Br^- ion pair in the cluster will be discussed, as will calculated infrared spectral and ionization potential signatures for its possible experimental detection. The acid-ionized $HBr(H_2O)_4$ cluster will also be considered in the context of its formation from less stable species via two routes: via addition of H_2O to an $HBr(H_2O)_3$ cluster and via HBr addition to a $(H_2O)_4$ cluster. Possible implications for the reaction on ice will be given.

If time permits, the HBr results will be contrasted with those [5] for HCl and HF in small water clusters.

This work was supported by NSF grants ATM-9613802 and CHE-9700419, and by a CIRES Visiting Fellowship, 3/1996–2/1997 (BJG). Acknowledgment is made to the National Center for Atmospheric Research, which is supported by the NSF, for computing time used in this research.

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[5] B. J. Gertner and J. T. Hynes, to be submitted.

TALK 43
Wednesday 15.20 - 15.50

« Spectroscopy of H_2O+ »

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While photoelectron spectroscopy on water shows the three electronic statues $\tilde{X}$ 2B1, $\tilde{A}$ 2A1 and $\tilde{B}$ 2B2, high resolution spectroscopy has been carried out only on the two lowest $\tilde{X}$ and $\tilde{A}$ states, which are the two Renner-Teller components of a 2u state that the cation would take in a linear configuration. The wide variation between the equilibrium geometries of these states leads to an extensive vibrational band structure of the electronic transitions.

The first detailed rotational analysis of the $\tilde{A}$ - $\tilde{X}$ emission spectrum, recorded on photographic plates, was published more than twenty years ago. Subsequently, far-infrared and infrared laser spectroscopies have given precise information for the lowest vibrational levels of $\tilde{X}$ 2B1. More recently, emission Fourier transform spectroscopy and near-infrared laser measurements have extended the observed rovibronic energy pattern for both the two lowest electronic states, which is particularly complicated in $\tilde{A}$ 2A1.

A brief review of the data resulting from these different experimental techniques will be presented and discussed.

Pavel Rosmus

Theroetical Chemistry, UMLV, France

Variational Renner-Teller calculations for the linear/bent A^2A_1-B^2B_1 system has been performed using accurate ab initio potential energy, electric dipole, electronic transition moment and orbital angular momentum three-diemensional functions. An accurate barrier to linearity has been determined which lead to reassignments of all experimentally known vibronic levels in the A-state. Vibronic origins for H_2O^+, HDO^+ and D_2O^+ up to about 30000cm^{-1} have been calculated including also the spin-orbit split rovibronic levels up to K_a =5. Absolute absorption line strengths and radiative lifetimes were obtained from the ab initio electric dipole, electronic transition moment functions and variational rovibronic eigenfunctions. The theoretical data are in excellent agreement with available spectra and proved to be very useful in assignments of new transitions of this ion. The theoretical treatment of the Renner-Teller problem used in this study is the most complete, to date.

POSTERS

« Theoretical Study in the Infrared (IR) Spectra of the Hydrated 7-Azaindole clusters 7-AzI$(H_2O)_n$ »

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With the ab initio molecular orbital (MO) method, structures of the hydrated 7-azaindole clusters 7-AzI$(H_2O)_n$ were optimised and their normal frequencies were calculated to analysis the infrared spectra (IR) obtained with the experimental technique by Fujii and co-workers. The molecule of the 7-azaindole is a condensed ring consisting of the six-membered pyridine ring and five membered pyrrole ring, and can make the complex with water molecule at both acid and base part with hydrogenbonds.

Up to n = 3, the experimental spectra have a interval region between symmetric stretching modes and antisymmetric stretching modes of water molecules. The most stable isomers of 7-AzI$(H_2O)_n$ for $n \leq 3$ has single ring structure constructed through the hydrogen bonds. Especially single ring isomer of 7-AzI$(H_2O)_2$ is stable because of small structural deformation. The calculated IR spectra of the single ring isomers are mostly good agreement with the experimental spectra.

The interval of IR spectra between symmetric and antisymmetric stretching modes of water molecules is seen in the several clusters of the hydrated organic molecule such as phenol-$(H_2O)_n$, benzene-$(H_2O)_n$, and tropolone-$(H_2O)_n$. In these clusters, the interval region is also attributed the single ring structure of hydrogen bonds. The behaviour of the normal frequencies of water molecules can be explained with the simple model of the coupled oscillation system.

For $n \geq 4$, the most stable isomer of 7-AzI$(H_2O)_n$ is the complex of 7-azaindole and pure water cluster $(H_2O)_n$. These larger clusters, however, can easily dissociate to 7-AzI molecule and $(H_2O)_n$ clusters. In the experimental spectra of n = 2, the absorption bands are obviously appearing more than expected theoretically. The peak location of tne extra bands are corresponding to the normal frequencies of the water clusters $(H_2O)_n$. It is seemed that considerable reason for the IR spectra of n = 2 is the pure water clusters $(H_2O)_n$ dissociated from the larger clusters of 7-AzI$(H_2O)_n$, and observed together with the stable single ring isomer 7-AzI$(H_2O)_2$.

POSTER 2

« The Spectroscopic Properties of Water Clusters: Relevance to Atmospheric Radiative Transfer »

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Department of Physical Chemistry and The Fritz Haber Research Center, The Hebrew University, Jerusalem, Israel.

The effect of water clusters upon atmospheric radiative transfer in the infrarered and visible have been examined. Structures and vibrational frequencies from the literature were used to compute equilibrium constants for $(H_2O)_n$, n = 2, 3, 4. Experimental spectra are used to bracket the infrared and visible intensities of vibrational overtone and combination bands arising from hydrogen bonding in water clusters. Vertical profiles of temperature, pressure and humidity are used in conjunction with the equilibrium constants to obtain abundance profiles of the dimer, trimer and tetramer. The radiative effects of these clusters were obtained with a line by line radiative transfer model of the propagation of sunlight through clear and cloudy atmospheres to the Earth's surface.

POSTER 3

« Ar Induced Halfwidths and Line Shifts of Water Vapor Transitions »

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Pressure-broadened halfwidths and pressure-induced line shifts are determined for water vapor transitions with argon as the perturbing gas. Calculations based on the Complex Robert-Bonamy (CRB) formalism are made for a number of vibrational bands for which there are experimental data to compare with. The intermolecular potential is taken as a sum of Lennard-Jones (6-12) atom-atom, isotropic induction, and dispersion components. The dynamics of the collision process are correct to second order in time. None of the molecular constants have been adjusted to give better agreement with measured halfwidths or line shifts. The convergence of the atom-atom potential for this system is investigated and it is found that a 12^{th} order expansion of the atom-atom potential in needed. A new feature in the CRB approach is that the real and imaginary components of the S matrix affect both the halfwidth and the line shift. It is shown here the imaginary parts of the S matrix strongly affect the calculated H_2O-Ar halfwidths. The results are compared with the measured values and with previous calculations. Good agreement is observed between these calculations and the measured values for both halfwidths and line shifts. It is also clear that some parameters describing the intermolecular potential need to be better determined.

« Measured and calculated broadening and shifting in the ν_2 water vapor band »

A. Valentin, Ch. Claveau

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A.D. Bykov, N.N. Lavrentieva, V.N. Saveliev, L.N. Sinitsa

The Institute of Atmospheric Optics, Tomsk, Russia

Self and N_2 line broadening and shifting of the H_2O ν_2 band have been studied in the 1850-2230 cm^{-1} region.

The measurements were made with the Fourier transform spectrometer at the Laboratoire de Physique Moléculaire et Applications of the University of Paris (for 70 lines).

Fourteen spectra at different pressures of gaz mixtures ($p(H_2O)$) between 0.75 and 12 torr, $p(N_2)$ between 0-400 torr) have been recorded in the temperature region (258-299 K). The spectral resolution was chosen equal to 0.005 cm-1.

Accuracy in the determination of the line shift coefficients was estimated to be better than 1mK/atm (1mK = 0.001cm^{-1}).

The line center position and width determination were made by nonlinear least square fitting, assuming a Voigt line profile, to the measured values of transmittance. The lineshifts and linewidths have been determined by fitting to measured line position and width values for the different pressures of samples.

Calculations of self and N_2 induced lineshifts coefficients were performed using the Anderson-Tsao-Curnutte theory considering dipole-dipole (for self-induced pressure shifts), dipole-quadrupole, quadrupole-quadrupole, induction and dispersive interactions. Fairly satisfactory agreement between measured and calculated lineshift coefficients has been found.

Self induced pressure broadening and shifting were estimated from data at 0.72-12 torr H_2O pressure. The temperature dependance of lineshifts and widths coefficients is discussed.

The authors from Tomsk acknowledge the support by Russian Foundation for Fundamental Research (grants N° 98-02-17772 and N° 98-02-16375). This study have been performed in the framework of Programmes Internationaux de Coopération Scientifique (PICS) N° 591.

POSTER 5

« The TCPE many-body model for water »

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Several quantum chemistry studies have exhibited that cooperative effects strongly reinforce the stability of hydrogen bonding patterns where each molecule is simultaneously donor and acceptor of hydrogen bonds. These topological properties of cooperative effects (which may easily interpreted using charge transfer concepts) have been considered to built a new flexible many-body model for water (the TCPE model). The TCPE interaction energy is decomposed into five terms : repulsive, charge-charge, intramolecular relaxation, polarization and hydrogen bonding. The polarization term is taken as a classical molecular many-body polarization potential. The hydrogen bonding term is also a many-body potential and it is introduced to reproduce for the topological properties of the cooperative effects occurring in water. TCPE parameters are derived from ab initio calculations at the MP2/6-311+G(2df,2p) level on three water dimer structures and on the cyclic water trimer, and from recent experimental results in the gas phase regarding the OH stretch vibrational spectra of small water clusters (from 2 to 5 molecules) TCPE has been applied to the study of small water clusters $(H_2O)_n$ (from n = 3 to 20) and it has shown that this model is able to closely reproduce both theoretical and experimental results regarding such clusters.

POSTER 6

« Temperature Effect on the Water Vapor Continua Absorption in Various Gas-Phase Mixtures »

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The nature of the water vapor continuum absorption in natural atmosphere is still controversial. Great deal of attention is paid to the modeling of non-lorentzian line profiles, especially far from the line centers. Also hydrogen-bonded $(H_2O)_2$ dimers and $H_2O...N_2$ complexes are discussed in the literature as possible carriers of continuum absorption in the infrared and mm-wave ranges. Significant breakthrough in experimental studies of mm-wave continua is marked by systematic investigations of the temperature dependence of absorption in pure water and its mixtures with N_2, CO_2, and Ar by A. Bauer et al. (see [1] and references therein). Several lineshape models were tested to fit the data of these experiments; none were found adequate to the whole set of measurements.

In the present work the water vapor continua in H_2O–H_2O, –N_2, –CO_2, or –Ar are attrubuted to dimers and weakly bound binary water complexes. The temperature dependence of absorption is determined mainly by mass-action law for relevant association reactions and can be reasonably evaluated accounting for effective dissociation energy decrease due to thermal ro-vibrational excitation. Relevant statistical physics theory is described in detail in [2-4]. The values of dissociation energies for $(H_2O)_2$, $H_2O...N_2$, $H_2O...CO_2$, and $H_2O...Ar$ are available from quantum-chemical calculations. The temperature dependence of continua is governed in our model by two fixed parameters per each molecular pair, which can be determined in the course of least square fitting of experimental data. In all cases measured data are reproduced within experimental uncertainty (see Fig. 1).

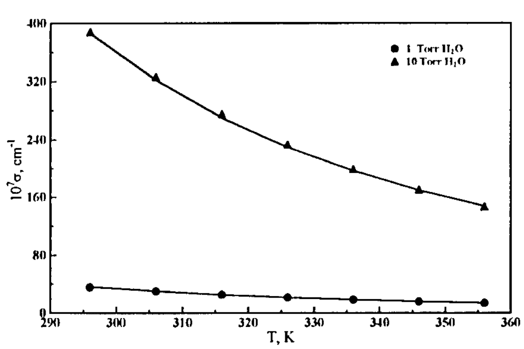

Fig. 1. Temperature dependence of continuum absorption in H_2O–CO_2 mixture at 239 GHz. Points are experimental data from [5] for 1 Torr and 10 Torrs water vapor partial pressure. The results of present calculations are shown by solid lines.

Several advantages of this model over previous ones can be formulated:

- A set of parameters, found in the course of our fitting, has clear physical meaning,
- The temperature and pressure dependencies in all mixtures are nicely reproduced using the same set of parameters for each molecular pair,
- The temperature dependencies of mm-wave and infrared continua in pure water vapor can be reproduced using the same set of parameters, these dependencies are notably different.

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Present consideration enables one to gain better description of experimental data using significantly reduced number of parameters. Moreover, this may give new insight into the nature of underlying phenomenon. A possibility is straightforward to build an ab initio theory of continuum absorption based on detailed understanding of molecular properties of individual weakly bound complexes.

The author is grateful to A. Bauer for supplying experimental data and fruitful discussions. Partial financial support from the Russian Foundation for Basic Research (project 96-03-34255) is acknowledged.

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POSTER 7

« Resonance ionisation spectroscopy of Phenol(H_2O)$_{6\text{-}12}$ Clusters »

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und K. Kleinermanns

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Using soft ionisation conditions we could obtain two-colour resonance ionisation spectra of phenol(H_2O)$_n$ with up to n = 12 water molecules and discriminate different isomers.

The analysis of the spectral shifts and the comparison of measured and *ab initio* calculated intermolecular vibrations have been used to investigate the structures of these multiple coordinated H-bonded systems.

The vibronic spectra of the n = 8 and n = 12 cluster in the spectral region of the n = 1 cluster are especially meaningful. The experimental data points to phenol H-bonded to (H_2O)$_8$ and (H_2O)$_{12}$ structures. This leads to the conclusion that clusters with a maximum number of planar (H_2O)$_4$ units reveal a special stability.

At least one more n = 8 isomer absorbs with high intensity spectral close to the n = 4 isomer.

Its spectral shift can be interpreted as an association of (H_2O)$_4$ to a phenol(H_2O)$_4$ unit.

Recently the vibrational spectrum of this n = 8 cluster was obtained using IR-UV double resonance spectroscopy.

POSTER 8

« DIFFUSION OF A CO_2 MOLECULE THROUGH A THICK WATER FILM PHYSISORBED ON MGO(100) »

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R.M. Lynden-Bell and T. Somasundaram

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The study of diffusion mechanisms of small molecules through water or ice layers is of fundamental interest for the understanding of many processes in atmospheric physics, environmental sciences and also in glaciology. Following the work of T. Somasundaram and R.M. Lynden-Bell describing the dissolution of CO_2 in a water film at 300 K [1], we have studied the perturbation of the diffusion process by the adsorption of the water film on the MgO(100) surface. Indeed, it is well established now that the water molecules form a first flat physisorbed monolayer on the perfect terraces of the MgO(100) surface that is stable even at ambiant temperature [2]. Moreover, the layering and the dynamics of the water overlayers is greatly influenced by the electric field created by this first flat layer of water molecules [3]. Therefore, we could expect that these more or less structured water layers would not behave as free water layers with respect to the diffusion of small pollutants.

We have calculated the free energy profile at T=300 K for a CO_2 molecule coming from the gas phase and diffusing through the adsorbed water layers following the Landau theory as:

$$\left(\frac{\partial A}{\partial z}\right)_T = \left\langle\frac{\partial U}{\partial z}\right\rangle_T = \left\langle F_Z\right\rangle_T$$

where A is the Helmotz free energy, U defines the total energy and z the distance between the molecular center of mass and the MgO surface. Therefore, the variation of the free energy with respect to z is equal to the average (in the canonical ensemble) of the z-component of the total force acting on the molecule. We have simulated by using molecular dynamics calculations, the trajectories of 164 water molecules and one CO_2 molecule, adorbed on MgO(100), in order to obtained $<F_Z(t)>_T$ and $A(z)-A_{vap}$ after integration.

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The results show that the structure of the water layers is considerably modified near the MgO surface with the formation of one flat monolayer covered by parallel bilayers up to 15 Å from the surface. The free energy of CO_2 exhibits a minimum at the gas-water interface (-5.6 kJ/mol), a strong energy barrier (6 kJ/mol) when the molecule enters the surface and a series of oscillations corresponding to the diffusion through the successive water layers. Finally, it is shown that a very stable site exists (-5.4 kJ/mol) in the first water bilayer (near the surface) and that a very strong barrier prevents any CO_2 crossing through this bilayer. The molecule thus appears strongly trapped into the water layers and cannot be adsorbed on the MgO surface. This results strongly differs from the previous one obtained for the free energy shape without MgO surface which has shown that the CO_2 molecule can cross through the last water layer and return to the gas phase.

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« On determination of the value of enthalpy change during hydration of ions in solutions. »

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The change of enthalpy at solvation of ions, DH, is an important fundamental quantity because it controlls the process of ion solvation, which, in its turn, controlls all ion processes in the solvatable surroundings. The conventional method of determination of DH values [1] consists in using the Born-Haber cycle, which comprises the dissociation of a compound in gas phase into cations and anions, the transfer of these ions from gas into solution, the solvation of these ions in the solution by solvent molecules and the recombination of these ions in solution. Application of Hess's law to this cycle results in the expression for total DH

$$\Delta H = \Delta H(c) + \Delta H(a) = -L(d) - \Delta H(cr) \qquad (1)$$

The value of L(d) (the heat of dissolving the compound) and $\Delta H(cr)$ (dissociation energy of the compound into ions in gas) are determined experimentally.

This method has two main disadvantages. The first, well-known one, is that the separation of the total ΔH into cation, $\Delta H(c)$, and anion, $\Delta H(a)$, components needs in additional assumptions, what results in unreliable results. The second disadvantage was not noticed up to-date: the whole value of ΔH accompanying the transfer of ions from unsolvated state in gas to solvated state in solution was ascribed to ion solvation in solution. However, the transition of an ion through gas-solution interface must be accompanied by a certain ΔH (the heat of condensation of the ion, W). Hence, the real value of the enthalpy change, $\Delta H(r)$, will be related to the corresponding tabulated value by the expression

$$\Delta H = \Delta H(r) + W \quad . \qquad (2)$$

For example, at hydration of sodium ions ΔH = -106 kcal/mol [1], the upper limit of W = -58 kcal/mol [2], therefore the lower limit of $\Delta H(r)$ = -48 kcal/mol. So, with due account of the heat of condensation, the tabulated ΔH decreased substantially. Similar situation may be also expected for other ions. Therefore, the conventional method of ΔH determination appears to be incorrect.

There is another method for separate calculation of ΔH values for cations and anions [3]. It uses the expression for a change of Gibbs's function, ΔG, at the transfer of an ion from vacuum into a solvent with dielectric permeability ε [4]:

$$\Delta G = -N(A)(ze)^2(1-1/\varepsilon)/2R \ ; \quad \Delta H = -N(A)(ze)^2(1-(1/\varepsilon)-(T/\varepsilon^2)(d\varepsilon/dT))/2R \qquad (3)$$

where (ze) and R are the charge and the radius of the ion, N(A) is the Avogadro number. However, this method also does not take into consideration the heat of condensation of ions. oreover, during derivation of (3), the $(d(\Delta H)/dT)$ and $(d\Delta S)/dT)$ values at constant pressure are, in fact, assumed to beequal to zero, which contradicts to expression (3). In other words, expression (3) is also incorrect.

At present, there is the experimental method for separate measurement of ΔH values for solvation reactions of cations and anions in solutions [5]. The method employs the evaporation of ions from solutions by means of a strong electric field followed by mass spectral analysis.

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POSTER 10

« Structure and Thermodynamics of $H^+(H_2O)_n$ ($n \leq 40$), and the Dynamics Following Electron RECOMBINATION »

Marcus Svanberg and Jan B.C. Pettersson

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We present a simulation study of the properties of isolated $H^+(H_2O)_n$ clusters, with size $n \leq 40$, and the dynamics of those clusters induced by recombination with free electrons. The thermal properties of the charged clusters are investigated by Monte Carlo simulations [1], using an empirical polarizable rigid water model together with a proton based description of the charged unit [2]. We study the structural differences between the solidlike and liquidlike phases of the clusters in the range 0 to 300 K. The transition between these two phases is particularly distinct in $H^+(H_2O)_{21}$ which attains the dodecahedral cage configuration at temperatures up to 150 K, a structure that does not survive above 170 K. The results support the idea that the "magic number" behaviour of $H^+(H_2O)_{21}$, i.e., the enhanced intensity of this cluster relative to neighbouring sizes as observed in experimental mass spectra [3], is restricted to temperatures below the melting point. We estimate the melting temperatures for $H^+(H_2O)_9$ and $H^+(H_2O)_{21}$ to be 130 and 160 K, respectively. Comparison with a neutral $(H_2O)_{20}$ cluster reveals that the melting process in the protonated clusters appears to be governed mainly by water-water interactions.

Molecular dynamics simulations are applied to study the second step in the sequence $H^+(H_2O)_n + e^- \rightarrow H(H_2O)_n \rightarrow H + mH_2O + (H_2O)_{n-m}$. The neutralization step is considered as a vertical process, by switching instantaneously from the ionic to the neutral ground state potential energy surface (if the transition is energetically allowed), with the nuclear coordinates frozen. Electronic excitation, as well as H_2O vibrational excitation, is thus neglected and we apply a purely repulsive H-H_2O potential. Our model can thus be considered as a limiting case, where a large amount of initial potential energy is rapidly transferred to *inter*molecular modes, thus enhancing the "dynamic" character of the process. The nascent $H(H_2O)_n$ cluster can be characterized by strong repulsive forces, and for $n = 21$ an excess energy of approximately 3.0 eV is made available upon neutralization. The H atom is ejected from the cluster within 50 - 100 fs, with a kinetic energy of 0.2 - 0.4 eV. Although the reminder of the released energy is absorbed by the cluster, less than one water molecule is typically ejected within 10 ps, allowing for complete intermolecular energy redistribution. While this first molecule carries a hyperthermal translational energy of ~0.2 eV on the average, subsequent fragmentation should proceed in an evaporative fashion from a thermally excited cluster.

The trajectory results indicate that for clusters larger than $n \approx 21$, only a minor fraction of the released energy will induce short-timescale hyperthermal fragmentation. This information simplifies the estimation of the degree of fragmentation of $H^+(H_2O)_n$ clusters, which is needed in the modelling of ion-induced nucleation of polar mesospheric clouds [4].

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POSTER 11

« Photodissociation of H_20: potential energy surfaces and nuclear dynamics. »

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3D adiabatic potential energy surfaces and transition dipole moments of nine excited singlet states of the water molecule have been calculated using the MRD-CI method for a wide range of nuclear configurations. These surfaces correlate to different electronic states of the OH radical.

Avoided crossings between the X^1A_1, B^1A_1 and D^1A_1 surfaces were investigated and approximate diabatic surfaces were constructed. The nuclear dynamics on these surfaces was studied with wave packet methods using a parallel computer program on an IBM SP.

We obtained absolute and partial cross-sections for dissociation to the various fragment states.

POSTER 12

« Water Cluster Approach To Study H-Bond Pattern in Liquid Water: Ab Initio Orientational Defects in Water Hexamers. »

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We perform a quite exhaustive ab initio search of the total potential energy surface (PES) of water hexamer that is reliable at the 6-311G(d,p) computational level. This search reveals 15 lower-lying water hexamer structures distanced by 1.75 kcal/mol from the global minimum attained by prism I structure. Counting on the zero-point vibrational energy, the actual order of these structures is the following. Two prisms including prism I occupy two lowest energy minima on PES. The next four structures of cage type fall in the interval of 0.56 to 0.64 kcal/mol above prism I. Their calculated rotational constants are in a good agreement with those reported by Saykally et al. [1]. The next hexamer is a chair. It lies above the lowest cage I by ca. 0.2 kcal/mol. The absolutely new structure of propeller type follows a chair. It distances from chair by 0.24 kcal/mol. The pre-opened prism structure with rather large total dipole moment of 4.4 D is the next structure. Three different prisms III-V then densely occupy then the energies around 1.375 - 1.376 kcal/mol. Another cage V structure lies above prism I by 1.7 kcal/mol. Boat hexamer is found between these prisms III-V and cage V. Book-type structure closes this energy scale at 1.74 kcal/mol above the global minimum.

Three novel lower-energy local minimum structures of water hexamer cluster are also found in this study. Their quintessential feature is that they are all five coordinated, i. e., they possess such pair of the oxygen atoms that is separated by the distance less 3.5 - 3.7 A, the position of the first minimum of the radial distribution function gOO of liquid water that defines in fact the boundary of the first coordination shell, and not interbonded through by hydrogen atom. Such pair of the oxygen atom form a "dangling" bond. These structures resemble a well-known Bjerrum-type orientational defect although they correspond in fact to some local lower-lying energy minima on PES of water hexamer. Formation of a "dangling" bond promotes appearance of nonlinear H-bonds between water molecules losing the tetrahedrality pattern. In particular, some O-O-O bond angles are clustered around 60° demonstrating that the corresponding water molecules are settled in nontetrahedral directions. Harmonic vibrations of these five-coordinated "patches" are thoroughly assigned. Calculation of their enthalpy and entropy shows that at room temperature the energy of formation is in the range of 2 - 2.5 kcal/mol. These five-coordinated "patches" are actually the first evidence of the theoretical ab initio existence of orientational defects in water clusters.

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« Water Cluster Cations as a Source of Hydrated Proton and OH Radical. »

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Neutral and positively ionized water clusters $(H_2O)_n$ and $(H_2O)_n^+$ with n<6 were analyzed consistently: the structures were optimized at the unrestricted Hartree-Fock level with 4-31++G** basis set, and then, the energy characteristics were obtained in the second order of the Moeller-Plesset perturbation theory. The optimal neutral structures served as the starting approximation for the configurations of cluster cations. This allowed us to consider the final cationic structures as a result of the actual relaxation processes that take place in water upon its ionization.

In all cations, H_3O and OH fragments can easily be distinguished. H_3O looks always like a distorted H_3O^+ ion, while OH resembles OH radical. According to the mutual arrangement of these fragments, the cations can be divided into two groups: in one group, the OH fragment exclusively acts as a proton acceptor in the hydrogen bonds with the neighbors, while in the second group, it is directly bonded to the H_3O fragment. In the first group structures, the H bond between OH and the neighbor H_2O fragment weakens as the cluster increases, and the external effect of about 0.4 eV may be sufficient for their dissociation onto a protonated water cluster and a free or quasifree OH radical.

The estimated adiabatic ionization potentials of non-chain-like clusters of the same size are almost equal and by about 0.5 eV higher than those of the chain-like clusters. Moreover, they decrease linearly with 1/n, and the extrapolation to an infinitely large cluster provides the value of 8.6 eV, which can be considered as the electron work function of liquid water. This estimate is close to the experimental photoelectric thresholds of water (9.39 (0.3 eV) [1] and amorphous ice (8.7 (0.1 eV) [2]. The solvation of the knocked out electron by an adjacent neutral cluster decreases the value by about 3 eV, and one may conclude that the energy of about 5.7 eV is sufficient for the ionization of water. In fact, the photons of 6.5-6.8 eV most efficiently initiate the photoconductivity of ice [3]. Similar processes can take place in water droplets in the atmosphere.

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POSTER 14

« Mass Selective Anion-ZEKE spectroscopy of the iodine water cluster. »

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Negativly charged halogen water clusters are interesting systems for several reasons. On the one hand, they play an important role in solutions as well as in atmospheric chemistry. On the other side, molecular anions allow access to neutral systems after stripping an electron. These neutral systems may be radicals, short lived intermediate complexes or weakly bound molecular systems. For instance, photoelectron spectroscopy of chemical reactions may deliver new kind of molecular and chemical information [1]. Our anion formation is performed by laser induced photoelectron emission from a metal surface very near to the orifice of a pulsed supersonic molecular beam nozzle. A large manifold of different anionic molecular species as well as very good cooling even of reaction products in the beam is the special feature of our anion source [2,3].

Iodine water clusters have been investigated intensively for studying solution effects in heterogeneous anionic and neutral water clusters. Despite numerous theoretical publications about halogen water clusters, the only spectroscopic experiments on such systems in the isolated gas phase have been low resolution photoelectron spectra for long time [4]. The first high resolution work on these systems are anion-ZEKE photoelectron spectra (information about the neutral cluster) [3] and predissociation spectra (information about the anionic cluster) of $I^-(H_2O)$ [5,6]. We present mass selected and high resolution anion zero-kinetic-energy (ZEKE) photoelectron spectra of $I(H_2O)$. The spectra exhibit the typical iodine spin orbit splitting. Information about the structure of the cluster and about van-der Waals frequencies have been deduced. But also new questions about barriers between isomeric structures and van-der Waals binding energies, about the influence of tunneling effects, charge-transfer-to solvent and dipole bound states of these clusters have been raised. For further information we investigated $I^-(D_2O)$. In $I(D_2O)$ the rotational constants change dramatically and possible tunneling may be supressed. On the other hand, the $I(H_2O)$ stretching frequency is effected only slightly by deuteration. This may help to discriminate rotational and vibrational excitation in the anion-ZEKE spectra of $I(H_2O)$.

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« Is NaI soluble in water clusters ? »

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We have undertaken the study of solubility of salts in solvents at the microscopic level through the spectroscopy and the dynamics of NaI embedded in clusters of polar molecules: ammonia (NH_3), water (H_2O) or acetonitrile (CH_3CN). We present here results indicating that the charge separation process is not as straightforward to understand as expected.

In these experiments, NaI-(solvent)$_n$ clusters are prepared in a supersonic expansion, ionized by a one-color resonant two-photon scheme using nanosecond lasers and detected with a time of flight mass spectrometer.

When water is the solvent, large clusters up to n>50 can be observed, whereas for NH_3 and CH_3CN no clusters larger than 10 could be evidenced (see Fig 1). The first step in the ionization process is the excitation from the ground solvated (Na^+-I^-) ion pair state X to a covalent excited state A. If the two ions Na^+ and I^- becomes separated in the solvent cluster , the electronic transition A $\leftarrow$ X oscillator strengh decreases drastically. The experimental mass spectra seem to indicate that in the case of water clusters, (Na^+-I^-) remains at the same equilibrium distance as in the free salt, probably since the molecule stays at the cluster surface whereas for NH_3 and CH_3CN, the two ions may be separated and stabilized independently by solvation.

Femtosecond pump-probe NaI dissociation dynamics is sensitive to the structure of the clusters and lead to similar conclusions.

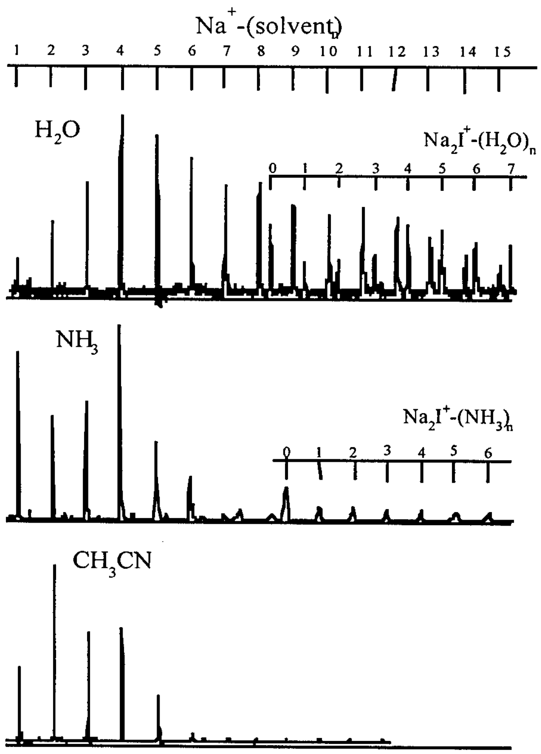

Figure 1 *: Na^+-(solvent)$_n$ mass spectra obtained after the excitation/ionization of NaI -(solvent)$_n$ clusters, the solvent being H_2O(upper), NH_3 (middle), CH_3CN(lower). A second series of peaks corresponding to Na_2I-(solvent)$_n$ is also observed. The mass scale is such that clusters having the same number of solvent molecules are one below the other. The three spectra have been recorded under similar experimental conditions : He backing pressure 3.5 bars, solvent partial pressure: p(H_2O)=100 torrs, p(CH_3CN)=400 torrs and p(NH_3)=300 torrs, laser wavelength 250 nm.*

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POSTER 16

« Measurement of atmospheric water absorption from 571 nm to 605 nm be intracavity absorption spectroscopy with an absorption path length of 300 km. »

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Intracavity absorption spectroscopy (ICAS) [1] with a multimode Rh6G dye laser is used to measure the spectrum of atmospheric water absorption with high sensitivity. The effective path length of absorption is set to Leff = c·t = 300 km by the duration of laser pulse, 1 ms. The laser emission is recorded by a spectrograph and a diode array at a combined spectral resolution of 2.4 GHz (0.08 cm^{-1}). The entire absorption spectrum in the range from 571 nm to 605 nm is constructed from individual overlapping emission spectra of 0.3-nm bandwidth each. The measured spectrum consists mostly of overtones of water vapour absorption. It is compared with a spectrum calculated from the HITRAN database with the absorptive path length being 300 km, and with adjusted humidity. All water vapor lines contained in the database are accurately reproduced in our measurements. This observation proves the feasibility of quantitative measurements of both spectral positions and strengths of weak absorption lines by ICAS. We have found also numerous unknown absorption lines which might be assigned to other atmospheric gases.

The outstanding potential of ICAS with respect to high sensitivity, high time resolution and high spectral resolution can be efficiently used to study smallest concentrations of water molecules e.g. in nanoclusters, in ionized and excited states, and to investigate their dynamics. ICAS allows the experimental simulation of the optical absorption spectra of planetary atmospheres. The longest effective length of the absorption path achieved so far by ICAS is 69,000 km [2]. Temporal resolution of ICAS measurements is limited only by the duration of the laser pulse, t0 = Leff/c, which varies proportional to sensitivity. The spectral resolution is limited, in principal, only by the spectral width of the oscillating laser modes, which is determined by the laser pulse duration.

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« Towards intermolecular potentials for flexible water molecules. »

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Developing intermolecular potentials for water dimers and small water clusters presents a difficult challenge to theory and experiment. Even for rigidwater molecules, there are six degrees of freedom in the dimer and this makes fitting of an accurate ab initio surface barely feasible. For larger clusters and for flexible water molecules, accurate and complete ab initio calculations are not possible.

Advances in the theory of intermolecular potentials now permit empirical potential energy surfaces to be calculated that are comparable with the best ab initio surfaces. One example is the SW1 potential [1]. This combines high-quality scaled SCF calculations of the electrostatic energy, an empirical model for the exchange-repulsion energy, published dispersion
energy coefficients and polarizabilities, and universal dispersion energy damping functions. The potential is roughly comparable in predictive power to the more widely used ASP potential [2].

Since the SW1 potential was published, there have been a number of new developments that can be used to improve its reliability and extend it to larger water clusters and flexible water molecules.

1. Writing two-electron integrals as an explicit function of orientation allows a functional form for the electrostatic and exchange-repulsion energy to be computed quickly and directly, from correlated monomer wavefunctions.

2. A new method for calculating exchange-induction energy using an effective exchange operator has been introduced and has proved extremely succeessful in modelling strong interactions, including dimers and larger clusters up to the solid state.

3. The damping functions which describe induction energy at short range are to be calculated using a model based on the relationship between molecular energy and charge density; this can be extended to non-pairwise interactions.

4. New scaling relations are available for the dispersion energy damping, which has previously been approximated by functions of doubtful validity.

The application of these methods to the flexible water dimer will be described, including a number of new results, and the progress towards a new SW potential will be reviewed.

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POSTER 18

« THEORETICAL CALCULATIONS OF ^{1}H AND ^{17}O NMR SHIELDINGS IN NEUTRAL AND CHARGED WATER CLUSTERS »

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Water is the most common liquid and solvent on Earth. The problems, associated with the properties of this common liquid, are not solved up to day despite the very thorough investigations with all available experimental techniques. The same is valid for the studies of aqueous solutions and behavior of water as solute in various media.

Recently, it was reported [1] that the ^{1}H and ^{17}O NMR chemical shifts of charged water clusters are independent of the charge of cluster, i.e. both negatively charged water clusters and positively charged water clusters exhibit deshielding relative to liquid (neutral) water. As this fact contradicts to the simple chemical logic, current theoretical investigation of neutral and charged (both positively and negatively) water clusters was undertaken by us. Calculations were carried out at the B3LYP/6-311+G** level of theory with full geometry optimization, and the chemical shieldings were calculated using GIAO method as implemented in Gaussian94 program package.

Our preliminary results agree with above given experimental findings. Factors responsible for such counterintuitive behavior will be discussed.

This research was in part supported by Estonian Science Foundation Grants #3361 and 3370.

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POSTER 19

« Structural, vibrational, and bonding analysis of M-OH_2 and HMOH (M=Li, Na; Be, Mg; Al, or Ga) using density functional theory. »

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The spectroscopic properties of the metal-water adducts and metal-water insertion interactions have been evaluated by a hybrid functional approach. The geometrical parameters, harmonic frequencies, and dissociation energies have been calculated for some of the alkai (Li and Na), alkaline earth (Be and Mg), and main group (Al and Ga) metals. The computed values show a good agreement with the few available experimental results. The bonding involved in the studied species have also been investigated using a topological method (Electron Localization Function). In the case of the metal-water molecular complexes, it is shown that the metal atom is essentially linked to the oxygen atom of H_20 by electrostatic interactions (dipole - dipole induced and quadripole - dipole induced). The minimization of the rr-repulsion is the cause of a tilted geometry. This process favours a small charge transfer from the metal atom to the ligand molecule. For the insertion complexes, the trrrns-structure is found to be slightly more stable than the cis-structure. In these complexes, the main group metal atoms show a trivalent character, in forming two covalent bonds with the oxygen and one of the hydrogens atomes.

POSTER 20

« Water vapor absorption in millimeter wave atmospheric windows ; continuums »

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Absorption in the atmospheric windows has received a great deal of attention in the last few years. It is known that models using only conventional line profiles of water vapor cannot reproduce the absorptions observed experimentally. The most widely accepted explanation is the inadequacy of impact lineshapes far from the line center. Absolute absorption studies have been performed in the laboratory, using a high sensitivity Fabry-Perot interferometer, with a high Q value (106). The method relies on measurements of the power loss factor of the gas. Most of the studies have been carried out at 239 GHz, between the 183 and 321-325 GHz H_20 lines. Following measurements for pure water vapor, systematic studies have been carried out for H_20-X gas mixtures at atmospheric concentrations, where pressure and temperature dependences were obtained and compared to different models . As the models using simple Van Vleck - Weisskopf or Zhevakin Naumov (Gross) lineshapes turn out to be very insuffiicient, various "continua", or derived lineshapes, have been derived by several authors for H_20-H_20 and H_20-N_2 [1]. They are mostly empirical or semi empirical ; a theoretical continuum has been obtained for pure water vapor from a quasistatic statistical approach. The agreement between experience and these models in generally satisfactory, but it appears that they do not always account for all the effects observed:

- excess of absorption (which can reach one order of magnitude for pure water vapor)
- strong quadratic component in the H_2O pressure dependence for H_2O-X mixtures
- strong temperature dependence

The choice of other mixing partners should allow a better understanding of the collisional processes involved. $C0_2$ has revealed to be a good candidate since it allows much larger effects than N_2 ; it is also of interest for Venus and Mars spectroscopic investigations [2]. The monoatomic gas Ar was also chosen as a mixing partner [3]. The H_20-C_2H_4 mixture is being studied. Results are also compared to collision induced absorption data in the same range.

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POSTER 21

« Quantum simulation of negatively charged water clusters and solvated organic molecules »

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We present results of Rigid Body Diffusion Quantum Monte-Carlo (RBDMC) calculations of the vibrational ground state of molecular clusters. The interaction of water with organic molecules will be presented using phenol-water as a model system. The relevant calculated properties are compared with experimental data.

Our method is then extended further to simulate dipole-bound cluster anions by combining the RBDMC with a rotationally adiabatic potential approximation1. A model calculation on the water dimer negative ion bound state is presented and compared to experimental electron affinities and ab initio calculations2.

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POSTER 22

« H/D-exchange reactions of cationized water clusters »

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Water clusters of the following general formulas can be formed by electrospray ionization: $M(H_2O)_n^+$, $M(H_2O)_n^{2+}$, $M(OH)(H_2O)_n^+$, $M(OH)(H_2O)_n^{2+}$; where M are different metals. The size of the clusters extend to more than hundred water molecules, depending on the conditions. When small clusters ($n < 10$) of this kind are allowed to react with D_2O at low kinetic energies in a tripelquadrupole mass spectrometer, exchange of intact ligands as well of H/D exchange can be observed. However, independently of the charge state H/D exchange is only be observed in the clusters which include a formal hydroxido ligand. In the clusters with only intact water molecule only exchange of intact ligands is observed.

A mechanism for H/D exchange based on proton exchange provide an explanations for these observations. I

POSTER 23

« Water Adsorption on the NaCl(001) Surface »

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Water adsorption on the NaCl(001) surface has been extensively studied both theoretically and experimentally during the last few years. Here adsorption is studied with potentials derived from InterMolecular Perturbation Theory (IMPT). The water model used is the recently developed ASP-W4 model. For the water-NaCl surface interaction, repulsion parameters were developed with IMPT and C_6 dispersion coefficients were calculated with the coupled Hartree-Fock approach. Structural optimizations of the energy minima and transition states have been performed for the water monomer, dimer, trimer, and tetramer on the NaCl surface. The water monomer has an interaction energy of -7.8 kcal/mol with the surface.The lowest dimer energy is 8.4 kcal/mol per water molecule and the lowest trimer energy is -8.6 kcal/mol per watermolecule. The water tetramer adapts a stable cyclic structure on the surface with a minimum energy of -9.5 kcal/mol per watermolecule. Optimizations of the watermonolayer on the surface have also been performed. For a coverage of one water for each NaCl unit two minima were found. A (1X1) water structure with an energy of -10.9 kcal/mol per watermolecule and a (2X1) water structure with an energy of -11.4 kcal/mol. For a coverage of two water for each NaCl unit a (1X1) minima was found with an interaction energy for each water molecule of -11.9 kcal/mol. Calculations with a coverage of 1.5 water molecules per NaCl unit are under way.

POSTER 24

« PHOTODISSOCIATION OF H_2O AND D_2O USING A TUNABLE "VUV LASER " »

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The photodissociation dynamics of H_2O in the second absorption band (120-140 nm) has been the focus of numerous experimental studies paralleled by theoretical developments. The dissociation proceeds directly or indirectly through the $\widetilde{B}\,(^1A_1)$ state, and can produce OH in both excited $(A\ ^2\Sigma^+)$ and ground $(X\ ^2\Pi)$ states. Experimental studies have concentrated on the measurement of OH products and on the detailed energy disposal. Analysis of the spontaneous $OH(A^2\Sigma^+)$ fluorescence, together with the existing theoretical studies provide a general picture of the energy disposal on the $OH(A^2\Sigma^+)$ fragments which are formed vibrationally cold with a highly inverted rotational distribution. The extremely high degree of rotational excitation has been explained as resulting from the large change in bond angle in going from the ground to the linear dissociative $\widetilde{B}\,(^1A_1)$ potential surface [1,2].

The objective of this work is to provide a complete determination of the rotational and vibrational distributions in the $OH(A^2\Sigma^+)$ (OD) fragments which results from the VUV photodissociation of H_2O (D_2O) in a number of wavelengths in the range corresponding to the second absorption continuum and to the region dominated by the strong molecular Rydberg transitions (117 and 132 nm). The photolysis laser is a tunable coherent VUV source based in a four-wave nonlinear mixing scheme [4]. Population distributions are obtained by analysis of the spontaneous fluorescence $OH(A^2\Sigma^+\rightarrow X^2\Pi)$ spectra using a fitting procedure based on a TSVD (truncated singular value decomposition) method, developed by Ruiz *et al.* [4] Our measurements confirm the general trends concerning the rotational distribution. The vibrational branching ratios on the contrary have to be revisited.

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POSTER 25

« Acid Ionized HBr in a Four-Water Cluster »

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In addition to its interest as a fundamental and important chemical reaction, the acid ionization — the proton transfer to a water molecule — of hydrogen halides in water is of environmental significance. Just as the acid ionization of HCl at the surface of ice is a key ingredient in the heterogeneous chemistry on polar stratospheric cloud particles in Antarctic ozone depletion mechanisms [1, 2], the acid ionization of HBr at the surface of ice plays an essential role in Arctic region atmospheric heterogeneous ozone depletion mechanisms [3].

In preparation for a theoretical study of the condensed phase reaction of HBr on ice, we have undertaken extensive quantum chemical studies [at the electron correlated MP2/6-31+G(dp) level of theory, and specially optimized variants thereof] of this molecule in small water clusters. In this talk, we will focus on the finding [4] that HBr is already acid-ionized in a cluster of as few as four water molecules. The structure of the H30+ Br– ion pair in the cluster will be discussed, as will calculated infrared spectral and ionization potential signatures for its possible experimental detection. The acid-ionized $HBr(H_20)_4$ cluster will also be considered in the context of its formation from less stable species via two routes: via addition of H_20 to an $HBr(H_20)_3$ cluster and via HBr addition to a $(H_20)_4$ cluster. Possible implications for the reaction on ice will be given.

If time permits, the HBr results will be contrasted with those [5] for HCl and HF in small water clusters.

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POSTER 26

« Nature and Importance of Three-body Interactions in Water Trimer : a Detailed Study of the Potential Energy Surface »

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Stationary points on the potential energy surface of the water trimer have been studied using highly correlated ab initio methods and semilocal density functional methods. The interaction energies corresponding to these structures of the trimer are decomposed into two- and three-body contributions. It is shown that the DFT results for the optimal geometries and the total interaction energies corresponding to these stationary points agree surprisingly well with the results of correlated ab initio calculations. By contrast, the DFT methods tend to overestimate the three-body contributions by ≈ 10%. The nonadditive three-body interaction energies have been analyzed using the symmetry-adapted perturbation theory (SAPT). The latter approach allows a decomposition of the interaction energy into contributions with clear, partly classical, partly quantum-mechanical interpretation, such as electrostatics, exchange, induction, dispersion and exchange-induction/exchange-dispersion cross effects. In all cases the induction term was found to be dominant, although it is partly canceled by the first-order exchange effects. The dispersion energy and exchange-dispersion cross-terms can be either negligible or significant depending on the geometry considered. Preliminary results suggest that the anisotropy of the three-body potential for the water trimer is a rather complicated function of the geometrical parameters of the trimer, and cannot be easily approximated by simple analytical models used in Monte Carlo/molecular dynamics simulations of bulk properties.

POSTER 27

« AB INITIO MCSCF STUDY OF THE BIFURCATED, INVERTED and LINEAR WATER DIMERS »

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The bifurcated (C2v), Inverted (Ci) and linear (Cs) water geometries have been optimized under symmetry constraint, at the MCSCF level. The various MCSCF Hessians have been computed and frequencies are reported for each type of water dimer. Without any BSSE correction, the bifurcated and inverted water dimers appear as saddle points, in agreement with previous MP2 studies (1). The possibility that the bifurcated and inverted water dimers might be local minima with a proper BSSE correction scheme (2) is discussed.

The bifurcated water dimer as well as the linear (Cs) Cis water dimer are considered for water dimer anions. Consideration of experimental Franck-Condon factors (3) suggests a bifurcated water dimer anion. Implications for a multi-attractor model of liquid water are also presented.

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POSTER 28

« Femtosecond Photoionization of $(H_2O)_n$ and $(D_2O)_n$ Clusters »

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We report on the femtosecond ionization at 780 nm of $(H_2O)_n$ and $(D_2O)_n$ clusters in a supersonic molecular beam that is coupled to a reflectron time-of-flight mass spectrometer. The use of femtosecond duration laser pulses for photoionization permits vertical excitation to the ionization state on a time scale which competes with excitation of nuclear motion. The high intensities (»1015 W cm^{-2}) utilized in this work give rise to ionization pathways distinct from nanosecond excitation processes. In fact, femtosecond laser pulses are producing large protonated $(H_2O)_nH^+$ clusters series, i.e.

$$(H_2O)_n + h\nu = [(H_2O)_n^+]^* + e^- = (H_2O)_{n-1}H^+ + OH + e^-$$

that are readily observable up to n » 60. The configurational energy imparted into the protonated cluster ion leads to metastable dissociation on the ms time scale:

$$(H_2O)_nH^+ = (H_2O)_{n-1}H^+ + H_2O.$$

This unimolecular decay on the ms time scale gives rise to intensity anomalies ("magic numbers") in the mass spectrum, which are interpreted by means of simulations of the ion trajectories in the mass spectrometer. The results are in agreement with the findings reported by using electron-impact ionization. Apart from the observation of large cluster sizes, two unique results of the femtosecond photoionization are disussed. First, the mass spectra show the presence of unprotonated cluster ions, $(D_2O)_n^+$, upon ionization of deuterium substituted water clusters which is in contrast to the previously reported near-threshold ionization at 11.83 eV. Second, in addition to singly charged cluster ions, doubly charged ions are observed, as will be discussed in this work.

POSTER 29

« SECOND TRIAD OF H_2O: NEW ANALYSIS OF VIBRATION-ROTATION SPECTRA IN THE REGION OF $\nu_1+\nu_2$, $\nu_2+\nu_3$, AND $3\nu_2$ BANDS AND CONFIRMATION OF HIGHLY EXCITED STATES FROM FLAME SPECTRA »

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The new analysis ofthe second triad of $H_2{}^{16}O$ (bands $\nu_1+\nu_2$, $\nu_2+\nu_3$, and $3\nu_2$) and the theoretical modeling of the upper ro-vibrational states (110)/(030)/(011) are presented, Infrared spectra have been recorded at room temperature in the range 4300-6300 cm^{-1} at resolutions between 0.008 cm^{-1} and 0.013 cm^{-1}. The use of fully evacuated transfer optics and a White-type multi-reflection cell [1] made large pressure x pathlength products possible (up to 26 mbar x 288 m). The high signal-tonoise ratio allowed us to observe lines having intensities as small as 10-26 cm^{-1}/mol cm^{-2} at T=296K. About 2300 lines have been assigned to the second triad and 580 upper state energies have been determined up to J=19 and Ka=10. The anomalously strong centrifugal distortion of ro-vibrational levels and resonance interactions have been accounted for using the generating function model [2,3], The RMS standard deviation of the least-squares fit of observed data was $8x10^{-3}$ cm^{-1}. The assignments of certain highly excited states have been confirmed by the analysis of flame spectra.

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POSTER 30

« Measurements on Water Vapor and Other Atmospheric Absorbers Using Intracavity Laser Absorption Spectroscopy »

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Accurate knowledge of water vapor absorption parameters are required for modeling the atmospheric absorption of water vapor. Water dimer is believed to contribute to the atmospheric near-IR absorption of water vapor. Thermodynamic calculations suggest that between 10^{-3} and 10^{-5} of the water vapor molecules in the atmosphere are in the form of dimers. Intracavity Laser Absorption Spectroscopy (ICLAS) is a high-resolution, high sensitivity technique capable of measurements of spectroscopic line positions, line widths and shapes, and absolute line intensities of weak absorbers with a sensitivity that far exceeds that of multi-pass absorption cells or Fourier Transform spectrometers.

ICLAS is based on the high sensitivity of a broad band laser to frequency dependent losses if the linewidth of the absorbing species is narrower than the spectrum of the laser. Very weak absorption lines of an absorber placed inside the cavity of a multimode laser can modify the laser spectrum and appear superimposed on the broad spectrum of the laser. The laser works like a multipass cell without losses for the detection of certain species. The effective path length of the system is the generation time multiplied by the speed of light multiplied by the fraction of the laser cavity occupied by the sample. With the appropriate generation times, path lengths on the order of hundreds of kilometers can be attained.

The system currently operating at the Massachusetts Institute of Technology employs a Ti:Sapphire laser that tunes in the 700-1000 nm wavelength region. This region includes absorptions due to the oxygen atmospheric bands (b $^1\Sigma_g^+ \leftarrow X\ ^3\Sigma_g^-$), water vibrational overtones, and peroxy radicals. Measurements on these species will be reported.

Acknowledgments
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« Theoretical Predictions of the Stabilities, Structures and Dynamics of Water and Proton-Water Clusters »

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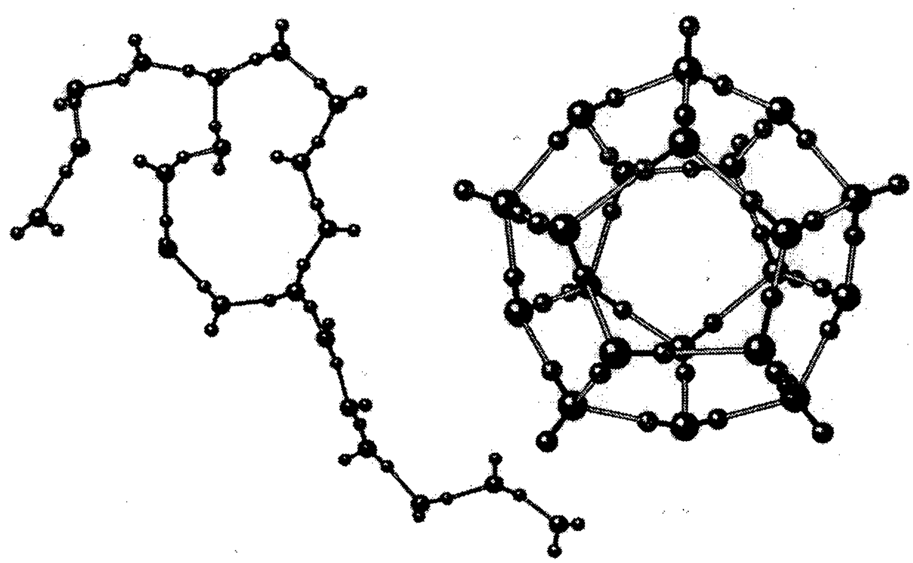
Investigations of neutral and protonated water clusters, $(H_2O)_n$ and $H^+(H_2O)_n$, using graph theory, quantum-chemical calculations and Monte Carlo or molecular dynamics simulations are described. An analytical potential model for water has been constructed, which allows for dissociation and includes polarization effects. It was derived by extensive *ab initio* calculations for the $H_5O_2^+$ ion, and subsequently applied in vibrational studies of $H_5O_2^+$ and in structural studies of larger clusters.

In order to systematically study the cluster structures, graph-theoretical techniques were applied to deduce all possible hydrogen bond topologies for a given cluster. Geometry optimizations using the graph-theoretical structures as initial guesses and the analytical potential model showed these to be local minima. Based on those results, empirical rules that govern the stability of the water clusters were infered, which aided in the further search for the global minimum. The structures of the minimum conformations were then confirmed by *ab initio* and density-functional quantum-chemical calculations. The water dodecahedral structure (n=20) and cube (n=8) have been studied in detail. It is shown that the hydrogen-bond topology is crucial for predicting their stabilities.

Molecular dynamics and Monte Carlo simulations for the protonated clusters show that when the temperature is increased a transition from closed to open, extended, star-like structures occurs.



POSTER 32

« Theoretical Study of the $OH\text{-}(H_2O)_n$ System »

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The structure and energetics of the anionic $OH\text{-}(H_2O)_n$ clusters have been investigated using various theoretical approaches. In particular, the nature and importance of the three-body interactions in the clusters of the hydroxide ion with water molecules, $OH\text{-}(H_2O)_n$, have been studied by several ab initio quantum-mechanical methods. For the dimer and trimer, benchmark calculations have been done at the MP4 and CCSD(T) levels, and compared with the results of (semilocal) DFT calculations, and symmetry adapted perturbation theory (SAPT) calulations. The latter approach allows a decomposition of the interaction energy into contributions with clear, partly classical, partly quantum-mechanical interpretation, such as electrostatics, exchange, induction, dispersion and exchange-induction/exchange-dispersion cross effects. The SAPT decomposition has been applied to characterize the nature of the three-body interactions for various geometrical configurations of the $OH\text{-}(H_2O)_n$ cluster (n = 2, 3, 4, 10) with water molecules located either in the first or the second solvation shell. In all cases the induction term is dominant, but is partly canceled by the first-order exchange energy, and the second-order exchange-induction and exchange-deformation effects. This suggests that the induction contribution is not a reliable approximation to the Hartree-Fock interaction energy. The dispersion and exchange-dispersion terms can be either negligible or significant depending on the geometry considered. This shows that the construction of simple analytical models for the three-body interaction potential of $OH\text{-}(H_2O)_2$ may be highly nontrivial. For $OH\text{-}(H_2O)_2$ the three-body energy represents only 5-7% of the pair interaction energy at the Hartree-Fock level, but it can reach as much as 22.6% for $OH\text{-}(H_2O)_4$.

« Structure of the water dimer anion and biomolecule-water anions »

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The water molecule is rather strongly polar (1.855 D) and the geometrical structure of water clusters is thus closely related to their respective resultant dipole moments. For example, the lowest energy configurations of the neutral trimer, tetramer, pentamer are rings with null dipoles while the dimer, with its *trans*-linear hydrogen bond, has a dipole of 2.65 D. Small molecules of biological interest such as isolated DNA bases or formamide which mimics peptide bonding, are also strongly polar molecules and their complexes with water possess large dipoles. It is possible to study these polar systems by taking advantage of a unique ionisation technique which allows for mass selection with negligible perturbation. Low energy electrons can be bound by the long-range dipole field of molecular systems as long as their resultant dipole is larger than a critical value of 2.5 D. The obtained anions ("dipole-bound anions") possess excess electrons in very diffuse orbitals and can further be field-detached by means of an externally applied electric field. The existence of magic numbers in the size distribution of water cluster anions is easily explained by the dipole configurations [1]. Water is also particularly interesting since it can lead to either rigid or floppy dimer anions whether it acts as a proton donor or a proton acceptor in an electron attaching neutral complex [2].

One of the conceptually simplest dynamic process occurring in a floppy microscopic system is the nondissociative electron attachment to a water dimer. Experimentally, we have studied $(H_2O)_2^-$ and $(D_2O)_2^-$ anions created by collisional transfer between laser-excited Rydberg atoms which play the role of a well-controlled source of very low energy electrons and neutral water dimers. By means of field-detachment spectroscopy, we have been able to observe intermolecular vibrations of these anions. A DFT calculation provides us the potential energy curves of these anions along two low frequency nuclear coordinates, the in-plane acceptor bend and the out-of-plane donor torsion modes. Large amplitude motions appear in the water and deuterated dimer anions [3]. The DFT calculation provides the excess electron distribution and electron affinities. The predicted vertical detachment energies are in very good agreement with those measured by photoelectron spectroscopy in the group of Bowen [4].

Hydration of DNA and proteins plays an important role in biology. We have determined the structure of complexes of water-DNA base and formamide-water complexes and their anions. The presence of a single water molecule strongly modifies their properties. For example, the electron attachment behaviour of Uracil or Adenine switches from dipole-binding in very diffuse orbitals to valence binding, leading to an important increase of the electron affinities, thermodynamical parameters which are crucial in mutagenic radiation-induced damages to DNA [5].

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POSTER 34

« UV Photodissociation of Water Clusters »

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The photodissociation of the monomeric gas-phase water molecule has been examined by a wealth of experimental and theoretical methods. Here, we describe our first results on the theoretical modelling of the UV photodissociation of water molecules within small (2 – 10 monomers) clusters of water.

Our work has first focussed on deriving a semi-empirical analytical potential for the excited states, on the basis of theoretical considerations and of *ab initio* computations at the RO-MP2 / 6-311++G(d,p) level of theory. Initially, this potential has been developed to describe the Franck-Condon region for excitation of the ground state cluster from the region of its minimum geometry, but work is underway to include the whole dissociation dynamics.

This potential describes the n excited states of the $(H_2O)_n$ cluster as linear combinations of diabatic states (and the corresponding diagonal matrix elements V_i), which themselves are described as clusters of n-1 ground state water molecules and one excited state molecule. The off-diagonal coupling elements V_{ij} between the diabatic states *i* and *j* depend on the coupling between the excitation dipole moments of the corresponding monomers. Diagonalisation of the matrix formed by the V_i and V_{ij} leads to the n potential energy surfaces.

More details on this potential will be given, as well as semiclassical absorption spectra based on the ground state quantum rovibrational wavefunctions.

POSTER 35

« Photofragmentation and structure of $Co(H_2O)^+_n$ and $Fe(H_2O)^+_n$ cluster ions »

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Gas phase studies of water clusters containing transition metals is important to unravel the solvation effects in inorganic and organometallic chemistries. We present here an experimental and theoretical work on $M(H_2O)^+_n$ cations, where M=Fe and Co, and $n \leq 10$, in order to give insight into the influence of the number of water molecules n on the structure of these ions.

Cluster ions are generated and selected using a machine which associates a laser evaporation source and a reflectron mass spectrometer. A laser operating at 532, 355 and 266 nm is used to photofragment the cluster ions, which provides photofragmentation cross sections at these three wavelengthes. In the case of iron containing clusters, a smooth variation of the cross section is found as n varies between 1 and 10. In contrast, a qualitative difference is found between the $Co(H_2O)^+_{\leq 6}$ and the $Co(H_2O)^+_{>6}$ clusters.

A possible interpretation is that cobalt cation inserts into an OH bond for the larger clusters. Ab initio and density functional (Becke3LYP) calculations are under progress. Preliminary results will be shown to examine this hypothesis. Based on these theoretical results for small ($n \leq 3$) clusters, relative solvation energetics of non inserted and inserted species have been estimated

POSTER 36

« Quantum Simulation of the Methanol-Water Complex »

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We use diffusion quantum Monte Carlo methods in a theoretical investigation of the van der Waals complex formed between water and methanol. As both molecules are capable of acting as either proton-donor or proton-acceptor, two distinct structures are possible for the dimer: a methanol donor form, $CH_3O\text{-}H\cdots OH_2$, and a water donor form, $CH_3HO\cdots H\text{-}OH$. Due to the small energy difference between them, there has been some uncertainty in characterising the strongest bound conformation. To date, both experimental and computational results vary, and current spectroscopic methods have been unable to observe both structures. Vibrationally averaged structures, bond energies and rotational constants for the two structures and several isotopomers of $CH_3OH\cdots\cdots H_2O$ will be presented and compared to the latest experimental results in an attempt to determine the lower-energy conformation and relative stability.

« The long-range interactions on H_2O molecule »

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Although there have been a lot of recent studies on the potential energy surface for the $\widetilde{X}\ ^1A_1$ ground state of the H_2O molecule[1-5], there is a lack of studies on the long range interactions on this system.

In the absence of those studies and mainly interested on the rovibrational spectra of water, the published potential energy surfaces don't reproduce the long range interactions or use a simplified form to emulate them. In particular, the recent potential energy surfaces of Varandas[3,5] neglect ``the intramolecular dependence of the atom-diatom dispersion coefficients". In addition, none of them aims to reproduce the electrostatic quadrupole-quadrupole interaction between the O-atom and the H_2 diatom that should dominate at long O-H_2 distances.

In contrast with this situation, the $O(^1D) + H_2(^1\Sigma^+_g) \rightarrow OH(^2\Pi) + H(^2S)$ reaction, which occurs mainly in this system, is believed to have a null activation barrier. So, the long range forces between the O atom and the H$_2$ diatomic should play an important role[6] on the dynamics of this important reaction in atmospheric and combustion chemistry. Despite that, this has been ignored in recent theoretical studies for this reaction[1,6,7].

In order to represent such interactions, we have done MCSCF *ab initio* calculations of quadrupole charge distributions, as well as for the dipole polarizabilities. Those calculations have been made for the different atoms and diatoms in their ground and first excited state as they appear as fragments on the water dissociation on a double-valued potential energy surface[8]. In particular, we study the (^3P) and (^1D) states of the O atom, the $(^2\Pi)$ and $(^2\Sigma)$ states of OH, and the $(^1\Sigma^+_g)$ and $(^3\Sigma^-_u)$ states of H_2.

Using those results we have been able to semi-empirically model the electrostatic, induction and dispersion energies that arises on this system when any of its components is far apart from the others.

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POSTER 38

« Giant Intermolecular Decay of Highly Excited Electronic States of Small Water Clusters »

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Highly excited electronic states of molecular clusters with intermediate-shell vacancies are calculated and analyzed using large scale *ab-initio* Green's function calculations. In sharp contrast to molecules, an *intermolecular* Coulombic mechanism has been found to lead to an ultrafast decay of singly and doubly ionized states of the clusters with vacancies in the inner-valence region. Small hydrogen-bonded $(H_2O)_n$ clusters (n = 2-4) have been selected as explicit examples to illustrate the pfoposed decay process, which does not occur in the H_2O-monomer. The decay mechanism and the main factors that exercise an influence on it are discussed. The corresponding decay widths are estimated in selected cases, showing that the lifetimes of the states are of the order of few femtoseconds. In addition, the generality of the proposed mechanism with regard to weakly bound systems is stressed.

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J. Zobeley, L.S. Cederbaum, and F. Tarantelli, J. Chem. Phys. (in press).

« Binding energy measurements of hydrogen-bonded complexes : the complexes of benzene and phenol with water and methanol »

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Accurate values for the binding energy between two molecules, in particular between organic molecules and water, remain very seldom data, despite their usefulness in order to validate the molecular dynamics models currently used in chemistry, biochemistry or molecular biology.

The present communication demonstrates the possibility to measure directly the binding energy of a hydrogen-bonded A-B complex, formed at low temperature in a supersonic jet. The technique is based upon the ability of the laser ionisation process to deposit substantial amounts of vibrational energy in the ionic complex A+-B. The experiment, carried out in a time-of-flight mass spectrometer, consists in detecting the fragmentation threshold of the ionic complex into twofragments A+ and B. This energetic measurement enables one to measure the 0 K binding energy of the neutral species A-B as well as, in some cases, that of the ionic A+-B species.
Thus the binding energy of two types of hydrogen bonds have been measured:

- one π-type hydrogen bond, in the benzene-H2O complex (2.44 ± 0.09 kcal/mol)

- two typical hydrogen bonds : those of phenol with water (5.60 ± 0.11 kcal/mol) and methanol (6.11 ± 0.18 kcal/mol).

In both cases the structure and the ionisation properties of these complexes have been modelled using a semi-empirical model in order to understand the origin of the vibration excitation induced by the laser ionisation.

Similar experiments carried out on molecules of biochemical interest, as DNA bases for instance, are envisaged in the near future.

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